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A theoretical study of the electronic structure of water

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A THEORETICAL STUDY OF THE ELECTRONIC STRUCTURE OF WATER

by

Frank O. Ellison

A Dissertation Submitted to the
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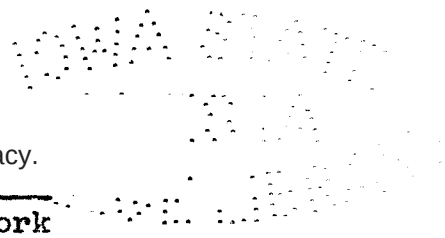

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TABLE OF CONTENTS

I. INTRODUCTION

A. Nature and Purpose of the Problem

The modern theories of molecular electronic structure are necessarily based on the principles of wave mechanics. Assuming that these principles are correct, the limitations which perpetually appear in problems of chemical valency may always be traced to formidable mathematical complications. The solution of these difficulties generally leads to an increased accuracy of description, but nearly always to a loss of conciseness and simplicity. The latter, on the other hand, constitutes one of the principal, although not always well manifested, designs of theoretical chemistry. Nevertheless, simple explanation, if it is to have the greatest degree of universality, must not only be supported by the primary measure of experimental verification, but also be capable of correlation with more rigorous interpretations. Oftentimes, this correlation becomes a valuable aid in devising more prolific simplifications.

The molecular orbital (MO) approximation is one of the important methods which is utilized for dealing with the problems of molecular quantum mechanics. It is simple in

the respect that it represents the natural extension of well-known atomic concepts to the molecular domain. In practice, the method has found a large degree of success on qualitative and semi-empirical grounds. Recently, C. C. J. Roothaan (1) has outlined a rigorous, yet straightforward, mathematical formulation of self-consistent field (SCF) MO theory. Into this, he has incorporated the linear-combination-of-atomic-orbitals (LCAO) approximation in a very generalized fashion. The SCF method secures the best possible wave function within the scope of the MO treatment. Most applications have been confined, however, to relatively specific areas where certain conditions of geometrical symmetry permit tractable computations. More general cases are certainly in need of consideration and solution.

It has been the first objective of this research to secure the best SCF MO wave function for the water molecule in the LCAO approximation. This molecule, although being the simplest of all common polyatomics, affords an exceptional insight into the physical laws of electronic structure. Thus, in the light of the foregoing comments, the secondary ends of the work have been to provide the following: (i) a means for a better understanding of the water molecule itself; (ii) a means to test the validity of the rigorous LCAO MO approach; and (iii) a means of

examining the limitations of simplified and related approaches to the solution of electronic structure.

B. Organization of the Thesis

The thesis is divided into four main chapters following this introduction. Chapter II is devoted to an exposition of the previous theoretical treatments of the water molecule and previous SCF MO treatments of other molecules. This same chapter is prefaced by a brief description of the approximations utilized in problems of electronic structure.

Chapter III is concerned directly with the SCF MO treatment of water. The first part describes the general mathematical application of the theory to this special case, and the second part gives the evaluation of integrals involved in the energy calculation. The estimation of three-center integrals constitutes the only approximation not inherent in the LCAO SCF MO theory which has been introduced into this treatment. Finally, the third part of this chapter relates and interprets the results of the calculations.

Chapter IV lists the major conclusions of the work, and Chapter V gives a brief summary.

II. REVIEW OF THE LITERATURE

A. General Considerations

1. The initial approximation

A molecule is here defined as any system of atomic nuclei and electrons. The problem of determining the electronic properties of such a system is the solution of Schrödinger's equation:

$$\mathcal{H}\Psi_f = \mathcal{E}_f \Psi_f , \qquad (2.1)^*$$

where $\mathcal{H}$ is the total electronic hamiltonian,** expressed in atomic units,# for the system of N electrons in the field of M nuclei held fixed in space; viz.,

$$\mathcal{H} = -\tfrac{1}{2}\sum_{\mu}^{N}(\nabla^{\mu})^2 - \sum_{\mu}^{N}\sum_{m}^{M}\frac{Z_m}{r^{\mu m}} + \sum_{\mu}^{N}\sum_{\nu>\mu}^{N}\frac{1}{r^{\mu\nu}} .^{\#\#} \qquad (2.2)$$

---

*Equations will be designated in this manner. The first number refers to the chapter, the second to the sequential position of the equation within that chapter.

**Magnetic effects due to the interaction of spins and orbital motions of the electrons will be neglected throughout.

#One atomic unit of length (a.u.) equals one Bohr radius, 0.5292 angstrom units (Å); one atomic unit of energy (a.u.) equals twice the ground state energy of the hydrogen atom, 2 x 13.602 electron volts (e.v.).

##Subscripts will generally be used to identify functions, superscripts to denote electrons and nuclei.

The function Ψ_f may be regarded as the electronic eigenfunction of the operator $\mathcal{H}$ corresponding to the state with the eigenvalue ε_f. Concern will be had only for this electronic part of the molecular wave function, the translational, vibrational and rotational parts being separated off (2, pp. 80-82, 190-192).

The starting point of the common approximation methods is the series expansion of Ψ_f in terms of more simple electronic state functions Ω_g:*

$$\Psi_f \approx \Gamma_f = \sum_g a_{fg}\Omega_g \,. \qquad (2.3)$$

The result Γ_f of such a summation will equal Ψ_f only if the series is carried over a complete set of functions. If the initial terms are chosen wisely, the convergence is expected to be rapid. Minimization of the energy,

$$E_f = \int \bar{\Gamma}_f \mathcal{H} \Gamma_f dv \,, \qquad (2.4)$$

with respect to the a_{fg} leads to the secular equation:

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*It should be noted here that approximations of Ψ_f are not limited to those leading to this type of expansion. By using complicated functions, with a sufficient number of variable parameters, very successful results have been secured for some simple molecules (cf. 3). Nearly perfect wave functions have thus been obtained without resorting to extremely long series. Such approximations are adaptable to the general case only with extreme complications.

$$|H_{gg'} - S_{gg'}E| = 0 \ , \qquad (2.5)$$

in which $H_{gg'} = \int \bar{\Omega}_g \mathcal{H} \Omega_{g'} dv$ and $S_{gg'} = \int \bar{\Omega}_g \Omega_{g'} dv$. This is solved for the roots, E, of which the lowest, E_f, determines an upper limit to ε_f. The coefficients a_{fg} corresponding to the variation function (2.3) are then determined by substituting E_f into the simultaneous equations from which (2.5) was derived.

The Pauli Exclusion Principle restricts the electronic states which actually occur to those corresponding to the eigenfunctions Ψ_f which are antisymmetric with respect to an interchange of any two electrons (2, p. 130). Therefore, the functions Γ_f, as well as the Ω_g's, must also have this property.

There are several properties of the eigenfunction Ψ_f which can be utilized in simplifying the choice of Ω_g's and facilitating the solution of (2.5). If a molecule has symmetry, the wave functions can be classified according to the irreducible representations of the symmetry group of the molecule to which they belong (4). Also, since the operators S^2 and S_z commute with $\mathcal{H}$ for all molecules, the eigenfunctions Ψ_f may be chosen so that they are simultaneously eigenfunctions of all of these operators (2, p. 233). Then, if the functions Ω_g are chosen so as to belong to symmetry species of the molecule, and to have definite

total spin and component spin angular momentums, the expansion (2.3) is considerably simplified. The a_{fg} will equal zero unless the Ω_g is identical with Ψ_f in these properties.

In the approximation methods under consideration, the basic electronic configuration wave functions which are utilized are always eigenfunctions of S_z. On the other hand, they are not necessarily eigenfunctions of S^2 nor members of irreducible representations of the molecule. The Ω_g's, which are taken to possess these properties, may be constructed from these basic functions as suitable finite linear combinations:

$$\Omega_g = \sum_h b_{gh} \Phi_h \ . \qquad (2.6)$$

Equations (2.3) and (2.6) now form the bases of the valence bond (VB) theory as well as the complete MO theory with configuration interaction (CI).* In the next two sections, a brief description of these two approximations will be undertaken.

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*Recently, Moffitt (5) has suggested a new approach to problems of electronic structure, based upon these same two equations.

2. The MO approximation*

This method, as was pointed out in the introduction, is an extension of the quantum mechanical treatment of atoms to molecules. This leads naturally to the identification of the functions Φ_h as antisymmetrized products (AP's) of one-electron molecular spinorbitals (MSO's). If the latter are denoted by the functions ψ_k, an MSO product wave function corresponding to a given N electron configuration may be written as follows:

$$\Lambda_h = \psi_1^1 \psi_2^2 \ldots \psi_N^N . \qquad (2.7)$$

This function is then antisymmetrized and normalized to give

$$\Phi_h = N_h \mathcal{A} \Lambda_h = N_h (N!)^{-\frac{1}{2}} \sum_p^{N!} (-1)^p P \Lambda_h , \qquad (2.8)$$

where N_h is the normalizing factor and $\mathcal{A}$ is the antisymmetrization operator as indicated. N_h is unity if the MSO's are orthonormal.

It is often necessary to take linear combinations of the Φ_h as indicated in equation (2.6). Then equation (2.3) expresses the basic MO CI approximation.

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*This description is largely drawn from (1) and (6).

One may now define the term electron shell, as used in MO theory, as

> . . . a set of MSO's in which (i) every MO occurs twice, namely, once with either spin, and (ii) if there is degeneracy on account of molecular symmetry, the MO's in the shell form a complete degenerate set (1, p. 71).

Most molecules have such a closed shell structure in the ground state, that is, in the lowest energy state in which the electrons have been placed in the lowest energy MSO's. Such a closed shell structure may be depicted as a single AP.* The true electronic state Ψ_f which corresponds to this closed shell structure should be reasonably approximated by this single AP:

$$\Psi_f \simeq \Gamma_f \simeq \Omega_f = \Phi_f . \qquad (2.9)$$

This should be moderately true only for a closed shell molecular ground state, since all other states of the same symmetry would be expected to be far removed in energy. For excited closed shell structures, it is very likely that CI would be of importance.

Assuming no spin-orbit interaction, which is, indeed, a very good approximation for light atoms, the MSO's may be separated into two factors. These are separately dependent upon space and spin coordinates, and written as follows:

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*A closed shell AP, Φ_k, is always totally symmetrical and singlet (zero total spin angular momentum).

$$\psi = \phi \begin{cases} \alpha \\ \beta \end{cases}, \qquad (2.10)$$

where α denotes spin of plus one-half and β spin of minus one-half. Two electrons with opposite spins may thus occupy one MO.

Equations (2.7) to (2.10) thus form the bases of the ordinary MO approximation. The specific formulation for the ground state of the water molecule is straightforward. The ten molecular electrons are placed in the five lowest energy MO's, so that equation (2.7) may be written:

$$\begin{aligned} \Lambda_o &= \psi_1^1 \psi_2^2 \psi_3^3 \ldots \psi_9^9 \psi_{10}^{10} \\ &= \phi_1\alpha)^1\phi_1\beta)^2\phi_2\alpha)^3 \ldots \phi_4\beta)^8\phi_5\alpha)^9\phi_5\beta)^{10}. \end{aligned} \qquad (2.11)$$

The problem is then to determine the formulations of the various MO's in order to secure closest correspondence of Φ_o with Ψ_o, the true electronic ground state eigenfunction.

3. The VB approximation*

This method is an extension of the approximation first

*This description is partially drawn from (2, pp. 232-240).

used by Heitler and London (7) for the two electron hydrogen molecule problem. The fundamental approach is one which is well suited to chemical description, inasmuch as the functions utilized are quantum mechanical analogues of common structural formulae. On the other hand, the method suffers in that it is difficult to apply with rigor, and has thus been restricted more than MO theory to qualitative and semi-empirical success.

The elementary functions used in constructing the Φ_h's* are the atomic orbitals (AO's) of the separated atoms which constitute the given molecule. The first step is to distribute the electrons among these AO's in a precise manner, viz., one electron in each bonding AO and two in each AO corresponding to a lone pair. The spins are assigned so that the total is equal to zero. The product of AO's with electrons thus assigned is then antisymmetrized so as to conform to the Pauli Exclusion Principle. These are the Φ_h functions of VB theory given in equation (2.6). For a given set of AO's, there will, of course, be several ways of distributing the electrons, and, therefore, several Φ_h's.

The formulation of the Λ_g's may be carried out in two steps, the first of which results in sets of functions

*Identical symbols for analogous functions in the VB and MO methods will be utilized. This considerably reduces the number of different symbols required. It will always be evident to which approximation they refer.

having the same eigenvalue of S^2, the second giving functions of correct symmetry. One takes linear combinations of the Φ_h's in such a manner that a change of sign results if two electrons forming a bond have their spin functions interchanged. This corresponds to the fact that the spin function associated with a stable bond is antisymmetric in the electrons. The final Ω_g's are determined by symmetry requirements. This method of constructing the Ω_g's will be clarified in its application to the water molecule (vide infra).

The electronic state of a molecule is represented as a superposition of the "structure" wave functions Ω_g according to the formulation of equation (2.3). This has special significance from the chemical viewpoint, inasmuch as it represents the state of a molecule not by any conventional formula, but by a "resonance" between several. The structures which are relevant to a singlet totally symmetrical ground state are only those which have just these properties.

B. Theoretical Treatments of Water

1. The classical electrostatic models

Before detailed consideration of the quantum mechanical treatments of H_2O, brief mention should be made of some

of the earlier theories in order to make this survey complete.

P. Debye (8) based his work on the conception of polar molecules as being systems having a distribution of electrical charge which could be characterized by a permanent electric moment. He considered H_2O as being made up of two protons and an oxygen ion. Utilizing formulae based upon atomic and molecular polarizabilities, Debye was able to consider the various possible geometrical configurations and determine which would be most stable. He was able to reduce the possibilities to two, each with an O-H distance of about one angstrom, one with an H-O-H bond angle of 64 degrees, the other, 110 degrees. The former gave a dipole moment of 1.34 D, the latter, 4.32 D. On this basis, he supposed the acute model to be the more probable.

Debye cites some previous investigations which are of historical interest. In 1916, W. Kossel (9) pictured the component atoms of H_2O as being hard spherical shells, thus leading to the conclusion of a linear model for the molecule. One year before he made his first formulation of the new quantum mechanics (10), Heisenberg considered H_2O (11) by a method in which the repulsive forces were introduced as power functions of the distance. In the same year, F. Hund (12,13) carried out a rather similar treatment.

2. The early quantum mechanical treatments

(a) VB treatments. Before specific consideration of the initial VB calculations on H_2O, it is wise to describe briefly a somewhat general application of the method to the molecule. In this way, the approximations which will be described may be more easily related and interpreted.

The common structural formulae of H_2O may be depicted and labeled as follows:

$$\underset{a}{H-O-H} \qquad \underset{b}{\overset{O}{H-H}} \qquad \underset{c}{H^+ \; O^{=}_{c'}-H \qquad H-O^{-}_{c''} \; H^+} \qquad \underset{d}{H^+ \; O^{*} \; H^+} \qquad (2.12)$$

Equation (2.3) may thus be written:

$$\Psi_o \simeq \Gamma_o = a_{oa}\Omega_a + a_{ob}\Omega_b + a_{oc}\Omega_c + a_{od}\Omega_d \quad .(2.13)$$

These are the functions which are to be constructed. They represent the most probable important VB structures which contribute to the ground state wave function.

The hydrogen 1s AO's to be utilized in the VB molecular functions will be designated h' and h". The oxygen functions will be designated 1s, ϕ_o, ϕ_1, ϕ_2 and 2px, the x-axis being perpendicular to the molecular plane. In the covalent structure Ω_a, ϕ_1 and ϕ_2 will be the bonding AO's.

The general designations allow for consideration of hybridized orbital representations of the form

$$\phi_i = \sum_p c_{ip} \chi_p , \qquad (2.14)$$

where the χ_p are oxygen AO's, say 2s, 2pz and 2py.* The functions ϕ_i will not be distinguished between the various VB structures, although such consideration would need to be made in actual application. That is, different hybrids would be involved in the different Ω_g-functions (17).

The first step is to construct all AO product functions Λ_h which are related to the above Ω_g's. The electronic spins in the 1s, ϕ_o and 2px orbitals are paired. Consider Υ_h as the product of AO's involving h', h", ϕ_1 and ϕ_2, and Θ as the product of the remaining lone pairs. The function ϕ_1 will be considered to be directed toward h', ϕ_2 toward h". Then,

$$\Lambda_h = \Upsilon_h \Theta$$
$$= \Upsilon_h^{1,2,3,4} \, 1s\alpha)^5 1s\beta)^6 \phi_o\alpha)^7 \phi_o\beta)^8 2px\alpha)^9 2px\beta)^{10}$$

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*In a more rigorous formulation, it would be found that this hybridization is equivalent to considering the interaction between several molecular states derived from atomic states differing in configuration but not in valence (14,15). In addition, there is the possibility of resonance involving excited state structures related to atomic configurations which differ in valence, an example being the contribution of $(2s)^2(2p)^2$ to the tetrahedral valence state of carbon (16).

$$
\begin{aligned}
\Upsilon_1 &= h'\alpha)^1\phi_1\beta)^2\phi_2\beta)^3h''\alpha)^4 \\
\Upsilon_2 &= h'\alpha)^1\phi_1\beta)^2\phi_2\alpha)^3h''\beta)^4 \\
\Upsilon_3 &= h'\beta)^1\phi_1\alpha)^2\phi_2\beta)^3h''\alpha)^4 \\
\Upsilon_4 &= h'\beta)^1\phi_1\alpha)^2\phi_2\alpha)^3h''\beta)^4 \\
\Upsilon_5 &= h'\alpha)^1\phi_1\alpha)^2\phi_2\beta)^3h''\beta)^4 \\
\Upsilon_6 &= h'\beta)^1\phi_1\beta)^2\phi_2\alpha)^3h''\alpha)^4 \\
\Upsilon_7 &= h'\alpha)^1\phi_1\beta)^2\phi_2\alpha)^3\phi_2\beta)^4 \\
\Upsilon_8 &= h'\beta)^1\phi_1\alpha)^2\phi_2\alpha)^3\phi_2\beta)^4 \\
\Upsilon_9 &= h''\alpha)^1\phi_2\beta)^2\phi_1\alpha)^3\phi_1\beta)^4 \\
\Upsilon_{10} &= h''\beta)^1\phi_2\alpha)^2\phi_1\alpha)^3\phi_1\beta)^4 \\
\Upsilon_{11} &= \phi_1\alpha)^1\phi_1\beta)^2\phi_2\alpha)^3\phi_2\beta)^4
\end{aligned}
\qquad (2.15)
$$

The AP configuration functions corresponding to each Λ_h are then written in the same manner as the MO formulation given in equation (2.8), namely,

$$\Phi_h = \mathcal{A}\Lambda_h \,. \qquad (2.16)$$

It is to be noted that the Φ_h's are not normalized, nor are they necessarily orthogonal to each other.

The Ω_g functions may now be written as in equation (2.6). The coefficients b_{gh} must be chosen so as to correspond to the various structures given in (2.12), that is, chosen so that each Ω_g is antisymmetric to interchange of

spins associated with a stable bond, as well as having appropriate symmetry.

The function Ω_a will involve Φ_1 to Φ_4, inclusive, as there are no possible combinations of the remaining functions which are antisymmetric to spin interchange of the bonding electrons (the spins of ϕ_1 and $\underline{h'}$, as well as of ϕ_2 and $\underline{h''}$, must be opposite). On interchanging spins of $\underline{h'}$ and ϕ_1, Φ_1 and Φ_3 interchange, and Φ_2 and Φ_4 interchange. On interchanging spins of $\underline{h''}$ and ϕ_2, Φ_1 and Φ_2, and Φ_3 and Φ_4 interchange. Therefore,

$$\begin{aligned} b_{a1} &= -b_{a3} \quad \text{and} \quad b_{a2} = -b_{a4} \ , \\ b_{a1} &= -b_{a2} \quad \text{and} \quad b_{a3} = -b_{a4} \ .^{*} \end{aligned} \tag{2.17}$$

These reduce to

$$b_{a1} = -b_{a2} = -b_{a3} = b_{a4} \ , \tag{2.18}$$

and

$$\Omega_a = 2^{-1} N_a (\Phi_1 - \Phi_2 - \Phi_3 + \Phi_4) \ .^{**} \tag{2.19}$$

Similar reasoning may be applied to the construction of the remaining Ω_g's. The structures $\Omega_{c'}$ and $\Omega_{c''}$ do not

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*These relations are obtained by inspecting equations (2.15).

**The factor, b_{a1}, equal to $4^{-\frac{1}{2}} N_a$, has been separated to simplify the normalizing factor. N_a equals unity only if the Φ functions are assumed to be orthonormal.

belong to the symmetry group of H_2O. Their sum and difference do, however. Only the former is totally symmetric, capable of entering into resonance in the ground state. The resulting functions may be thus listed:*

$$\begin{aligned}
\Omega_a &= 2^{-1}N_a(\Phi_1 - \Phi_2 - \Phi_3 + \Phi_4) \\
\Omega_b &= 2^{-1}N_b(\Phi_2 + \Phi_3 - \Phi_5 - \Phi_6) \\
\Omega_c &= 2^{-1}N_c(\Phi_7 - \Phi_8 + \Phi_9 - \Phi_{10}) \\
\Omega_d &= N_d\Phi_{11} \, .
\end{aligned} \tag{2.20}$$

The only purely theoretical VB calculations which have been carried out on H_2O are those by Coolidge (18), published in 1932. It should be emphasized that this was an approximate theoretical calculation; that is, it adhered to pure VB theory but utilized approximate AO's. All overlap integrals and multiple exchange terms were explicitly included, and all energy terms which arose from three-center interactions were accounted for. The computations were carried out for three values of the H-O-H bond angle.

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*The electron assignment in the Λ_h's as given in (2.15) defines the first term of the AP corresponding to each Φ_h. If a new $\Phi_{h'}$ were chosen which differed from the present choice, Φ_h, by an odd number of electron permutations, then $\Phi_{h'}$ would equal minus Φ_h. Therefore, the signs in equations (2.20) are naturally conditioned by the initial choice of Λ_h's.

Initially, the only functions considered were Ω_a and Ω_b, the final function being formulated as follows:

$$\Gamma_o = a_{oa}\Omega_a + a_{ob}\Omega_b \ .^* \qquad (2.21)$$

The results of the treatment are given in Table 1.

Table 1. Results of the VB calculation on H_2O[a,b]

H-O-H bond angle	a_{oa}	a_{ob}	Total molecular energy	Total atomic energy	Calculated dissociation energy
77° 22'	1.106	0.076	-18.4976	-18.3867	0.1109
90° 0'	1.082	0.083	-18.5133	-18.3867	0.1266
97° 11'	1.074	0.087	-18.5150	-18.3867	0.1283

a. Adapted from results of Coolidge (18).

b. All values are given in atomic units.

They may be considered to be very successful indeed, inasmuch as they predict a bond angle greater than 97 degrees, 11 minutes. Insignificant mention of this was made by Coolidge, since at that time the bond angle in H_2O was not known definitely. In 1933, Mecke and co-workers (19,20,21)

*The symbols used here are not those of Coolidge.

determined that the angle must lie between 102 and 111 degrees.

The observed dissociation energy for H_2O is 9.49 electron volts (22, p. 481), or about 0.35 atomic units. In order to secure improvement of the calculated results, Coolidge carried out an additional computation which included structure Ω_c. This led to a definite increase in the dissociation energy. The resulting normalized wave function for the larger bond angle was found to be

$$\Gamma_o = 0.7828\,\Omega_a + 0.0073\,\Omega_b + 0.3403\,\Omega_c\,, \qquad (2.22)$$

and the calculated binding energy was 5.7 electron volts, giving a depression of 2.2 electron volts by including Ω_c. The variation with respect to bond angle was little effected by this resonance.

The other early VB treatments were of a much more simplified and qualitative character. They were of great value, however, in establishing the quantum theory of directed valence. Pauling (23) first discussed the formation of H_2O in this sense, indicating that interaction between the two hydrogen atoms would lead to an increase in the bond angle. The latter effect would be enhanced because of the resultant positive charge on the hydrogen atoms attributed to the partial ionic character of the O-H bonds (24).

Heath and Linnett (25) have pointed out that Pauling's simple model is not able to account for the observed bond angle in H_2O. Using Pauling's value for the bond moment of the O-H link in H_2O, and the observed force constant for the H-O-H bond angle deformation, they are able to show that electrostatic repulsion between the hydrogens would open the bond angle to only about 100 degrees.

On the other hand, it should be noted that in addition to this resultant coulombic repulsion, there is an exchange repulsion between hydrogens which should be accounted for in the simple covalent VB model.

Slater (26,27) made some very simplified calculations on H_2O based upon semi-empirical VB theory. The assumption is first made that the structure Ω_a is sufficient to describe the molecule; that is, polar structures are not explicitly included. Secondly, the energy of the structure is determined under the assumption that all AO's are strictly orthogonal. This certainly appears to be unjustifiable inasmuch as bonds are considered to be formed between AO's which overlap as much as is energetically possible. However, the final formulation seems physically plausible, especially if one uses empirical values for the theoretical terms. For a bond angle of 90 degrees, Slater obtained a dissociation energy of 9.3 volts for H_2O. For a bond angle of 180 degrees, the result was 7.0 volts. It

was shown that the 2p valences by themselves have a definitely directional effect, but upon this is superposed an ordinary repulsion of the non-bonded atoms.

Van Vleck and Cross (28) obtained quite successful results for H_2O using semi-empirical VB theory. This treatment was very similar but more elegant than Slater's. Different and better empirical values were used for the necessary integrals. The energy equations were constructed primarily for the purpose of determining vibrational frequencies. They calculated a dissociation energy of 8.9 volts, but pointed out that any electron pairing theory of valence will predict a value approximately equal to twice the dissociation energy of OH. The computed frequencies are in remarkable agreement with theory: 3520, 3560 and 1660 wave numbers as compared to the observed 3755.8, 3651.7 and 1595.0 wave numbers (29, p. 281). In these calculations, the exchange repulsion between the hydrogen atoms was taken into account. This was accomplished by assuming that the resonance energy constitutes 0.88 of the total binding energy of a hydrogen molecule, and that a Morse function can be used to give the variation of this energy with distance. This calculation led to a minimum energy for H_2O at a bond angle of 100 degrees.

The early quantum mechanical treatments of H_2O, as well as those of other molecules, were very successful in

predicting the directional properties of bonds and thus geometrical molecular configurations. In the semi-empirical approach, the calculated results for dissociation energies seem astonishingly accurate in view of the quite radical approximations involved. This success is to be expected, of course, as Van Vleck and Cross (28) have noted. The simple VB energy formula is readily interpretable in terms of attractive bonding terms and repulsive non-bonding terms (30, p. 376). Empirical application is bound to give reasonable results, insofar as additivity of bond energies (and "non-bond" energies) is valid. A purely theoretical calculation based upon the simplified formulation probably would be much less encouraging.

The credit which is due to Coolidge's purely theoretical calculation is probably underestimated. With the inclusion of one ionic structure, which certainly should be included, the results are not too poor. They do, in fact, emphasize the need of introducing resonance. The simple theories supposedly obtain much better results without the need of such interaction. This is undoubtedly due to a hidden resonance included in the empirical constants derived from the OH molecule and utilized for H_2O. If one is concerned only with the simple energetics of the bond formation, this is probably a valid procedure. On the other hand, the principle bases of VB theory have been thus lost.

A general formula for molecular energetics, whatever its form, would indeed be interesting to have at one's disposal. It is doubtful whether such could exist without a more firm attachment to theory. In the case at hand, a semi-empirical VB method without explicit inclusion of resonance, seems to be contradictory.

A final point, and probably a very important one, should be made concerning the early VB calculations. In none of the treatments was any possibility for hybridization included. Especially for the water molecule, the effect of allowing 2s-2p mixing, or else the identical process of permitting resonance with an excited covalent structure, might be expected to be of considerable significance.

The problems cited here might be thought of as the ones which are of present day concern. More detailed analysis of these problems will be given later in this chapter.

(b) MO treatments. The early application of the MO method was directed primarily towards building up a conceptual scheme or qualitative theoretical framework into which empirical data, both chemical and spectroscopic, could be fitted. To aid in this course, rough LCAO approximations were often introduced, more for the sake of improving clarity, than of securing quantitative accuracy.

This LCAO formulation of an MO may be written as follows:

$$\phi_i = \sum_p c_{ip} \chi_p \ , \qquad (2.23)$$

where the χ_p's are AO's belonging to some or all of the component atoms and the c_{ip} are the LCAO coefficients. To a considerable extent, the latter are determined by symmetry and orthonormality conditions. Lennard-Jones (31) first introduced the LCAO scheme for diatomic molecules. Also, he utilized localized AO's for the molecular inner shells, a procedure generally followed in the subsequent MO treatments.

The general formulation of the electronic ground state configuration of H_2O was indicated in equation (2.11). This may be further qualified in the simple LCAO MO approximation as follows:

$$(1s)^2(2s)^2(\phi_y)^2(\phi_z)^2(2pz)^2 \ , \qquad (2.24)$$

where

$$\phi_y = a2py + b(h' - h'') \qquad (2.25)$$

and

$$\phi_z = c2pz + d(h' + h'') \ . \qquad (2.26)$$

The z-axis bisects the H-O-H bond angle and the x-axis is perpendicular to the molecular plane. The relations between the coefficients of the equivalent 1s hydrogen AO's, h' and h", are determined by symmetry.

F. Hund (32,33) was the first to show that such a model as this would have its equilibrium bond angle at 90 degrees. This result is obtained, however, by an oversimplified calculation (34).

Mulliken (35,36,37) utilized the simplified LCAO MO formulation of H_2O first of all to predict and assign ionization potentials (I's). The inner shell orbitals were supposed to have nearly the same I's as the valence state I's for the isolated oxygen atom. For example, the 2s localized MO would be estimated to have a "vertical" I* of about 32 electron volts and the 2px orbital about 14.7 electron volts (38). Actually, the latter is shown to be about 12.6 volts, the difference being attributed to a transfer of negative charge from the hydrogens to the oxygen, introducing extra electronic repulsion on the latter. For a bond angle of 90 degrees, it was estimated that ionization from ϕ_z should require greater energy than from ϕ_y (39). This supposition was based upon the fact that ϕ_z involves H-H bonding, whereas ϕ_y is H-H antibonding.

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*"Vertical" I's correspond to vertical lines drawn between potential energy curves. They refer to non-adiabatic I's in which the distances between nuclei remain unchanged during the process (Franck-Condon maximum of probability).

Mulliken predicted that these two MO's would be nearly degenerate or possibly reversed from the above order for the actual bond angle of 105 degrees (39,40).

Mulliken also established connections between relative electronegativities of atoms, LCAO coefficients, effective charges on atoms in partially polar molecules and dipole moments (41). On the basis of the greater electroaffinity of the oxygen atom, he assumed that $a/b > 1$ and $c/d > 1$ in equations (2.25) and (2.26). These inequalities were then considered to account also for the dipole moment of H_2O, the effective charges on the atoms being estimated from the latter as being roughly $(H^{+0.4})_2O^{-0.8}$. The molecular dipole was assumed to arise mainly on account of the polarity of the bonding MO's.

The fundamental MO approach to the electronic structure of H_2O was thus begun. Sound theoretical bases were still very far from being established, thus making the interpretations seem quite crude in nature. The latter, however, must not be allowed to obscure the real significance which the theory really possessed. A systematic understanding of molecular electronic structure was being developed, a step certainly comparable to Bohr's explanation of the hydrogen atom.

3. Recent advances

(a) General. Many significant advances in the general theory of molecular structure have taken place since World War II. Immediate attention was directed towards establishing the minimum number of simple, fundamental concepts so as to enable successful correlation of chemical experience.

Heath and Linnett (25) utilized the vibrational spectrum data of Darling and Dennison (42) to express the potential energy function of the H_2O molecule in terms of the distortions of the bond angle and lengths. They attempted to account for the various forces operating in the H_2O molecule by study and interpretation of the various cross and higher terms in this function. It was found that changes in 2s-2p hybridization are able to explain satisfactorily the signs of the cross-terms whereas repulsion between the hydrogen atoms is not a major factor in these respects. Furthermore, the coefficients of the cubic and quartic terms in the potential energy function appeared to measure only the departure of the bond dependence from the simple parabolic form. They closely resembled similar terms in the function for OH, and did not indicate any measure of interaction between the two bonds, the bonds and the angle, or between the hydrogen atoms.

In 1951, Linnett and Poë (43) carried out calculations of the electron configurations having maximum probability for the atoms in the first short period. These were secured by first setting up the Slater determinant (44) for the atom given a definite assignment of one-electron atomic spinorbitals. The AP was then squared and integrated over all spin coordinates leaving a probability function dependent only upon the spacial coordinates. The values of the latter which caused this probability to be a maximum were then found by differentiation or computation. Also determined were configurations of peak probability, that is, those which corresponded to a relative, but not an absolute maximum.

For the oxygen atom with the electron configuration

$$(1s\alpha)(1s\beta)(2s\alpha)(2s\beta)(2pz\alpha)(2pz\beta)(2px\alpha)(2py\alpha) \quad , \quad (2.27)$$

it was found that a configuration of peak probability existed in which there is a pair of electrons on the nucleus and two close pairs and two single electrons away from the nucleus arranged so that the total symmetry of the whole is C_{2v}. The symmetrically arranged single electrons are on one side of the nucleus, their plane being perpendicular to the plane of the pairs which are situated on the opposite side of the nucleus. The probable distances

from the nuclei were 1.1 atomic units for the pairs and 0.99 atomic units for the single electrons. The observed O-H distance in H_2O is 1.8103 atomic units (29, p. 489). The angle between the single electrons was found to be 103 degrees; between the pairs, 133½ degrees; and between a pair and a single electron, 104½ degrees.

Heath and Poe" stress that the nuclear configuration of H_2O may be expected to be related, to some extent, to this electron configuration of the oxygen atom. Thus, the unpaired electrons on the latter pass into the pairs in the molecular bonds, and it is likely that the directions will be close to the directions of the single electrons. This is similar to Pauling's supposition (23,45) that a bond will be formed in the direction in which the electron would most probably be found to its greatest extent.

Similar computations for neon, the united atom of H_2O, yield the expected angle between each of the four lone pairs to be 109½ degrees. The H-O-H bond angle, actually being 104½ degrees, is thus seen to lie between that for the united atom and the isolated oxygen atom. Heath and Linnett stress that the usual approach of assuming that the ideal bond angle is 90 degrees is illogical because it ignores all other electrons except the outermost valency electrons. Repulsion between the hydrogen atoms is comparatively unimportant (vide supra). This treatment, on

the other hand, is maintained to be equivalent to considering 2s-2p hybridization with the further refinement of explicit inclusion of the Pauli Principle.

It is somewhat difficult to secure a complete and satisfactory understanding of the paper by Linnett and Poë. The treatment is unconventional when compared to the usual approaches to molecular and atomic structure. There seem to be some apparent difficulties. For example, the authors consider only that configuration of the "ground state" of the oxygen atom in which the bonding electrons have parallel spins. Now, the ground state of the oxygen atom, having four electrons outside of closed shells, is not capable of expression in a single determinant. Secondly, the oxygen atom prepared for molecule formation is usually supposed to be energetically promoted to a valence state (38) in which there is a statistical distribution of spins in the bonding orbits. These factors possibly are not directly relevant to the present problem, but they certainly deserve some recognition and explanation. In this same connection, the treatment of Linnett and Poë is unique in that it makes no explicit recognition of the energy required and gained on molecule formation. Yet at the same time, the authors maintain that their method is equivalent to a study of hybridization. A VB treatment of hybridization generally requires either consideration of the

promotion energy to the hybrid valence state, or the equivalent study of the restricted resonance between various pure atomic valence states in zero hybridization (see footnote on page 15).

A critical survey of the method of ionic-homopolar resonance was published by C. A. Coulson (17) in 1951. This review discussed some theoretical difficulties and in addition cited some of the possible areas which merit further research. Also, there is a short discussion of the problem as applied to H_2O. There are two surprising results which are discussed. First, the contribution of the electric moment of the two lone pair electrons to the dipole moment is calculated to be 3.19 D. This turns out to account for the principal part of the electric dipole of H_2O. In the second place, ionic resonance in the O-H bonds is found to contribute the astonishingly small moment, 0.34 D. These figures are based upon very rough considerations, of course, but certainly serve to stimulate further study.

At the Shelter Island Conference on Quantum Mechanical Methods in Valence Theory, in September, 1951, M. Kotani (14) reported on an investigation of the VB approximation as applied to H_2O. The computations constitute a general study of the resonance in the ground state involving many possible non-ionic structures, or states. The approximations

which were included should first be enumerated: (i) overlap integrals between orbitals belonging to different atoms were neglected; (ii) semi-empirical values for the coulomb and exchange integrals were assumed; and (iii) direct interaction between the two hydrogen atoms was neglected. The results are important in that they roughly support the contention that the eigenfunction of a ground state can have rather large contributions from "excited" VB states. The latter may be states differing in the ordinarily assumed assignment of bonds as well as including the possibility of having two electrons in a bonding orbital.

Mulliken and co-workers (46) have discussed refinements of the MO theory as applied to H_2O. It is first recognized that bonding, as well as 2s-2p hybridization may occur in the orbital which was originally assumed to be a localized lone pair orbital of pure 2s oxygen character. In such an event, the bonding in ϕ_z will necessarily be weakened, but there will be an overall strengthening of the total molecular binding. The reasons for these facts may roughly be understood as being analogous to the resonance phenomenon which is continually encountered in VB theory. This reasoning thus seems to establish the order of energy of the MO's as follows:

$$1s)^2\phi_s)^2\phi_y)^2\phi_z)^2 2px)^2 , \qquad (2.28)$$

where ϕ_s indicates a nonlocalized MO largely composed of 2s character.

Mention should be made of a discussion by A. D. Walsh (47) to the effect that the order given in equation (2.28) is incorrect. It was contended that because of 2s-2pz hybridization, ϕ_z becomes essentially a non-bonding or lone-pair orbital. There are three observed I's for H_2O, of which only the first and third are observed spectroscopically as Rydberg Series (48,49,50). Walsh points out that strongly bonding electrons, such as those in ϕ_y, are not likely to give a series of discrete transitions.

These contentions are also supported by the fact, which was first pointed out by Mulliken (vide supra), that ϕ_y is H-H antibonding and, therefore, should probably be higher in energy than ϕ_z. This difficulty may be partially explained by two considerations. First of all, it can be shown that the energy of an MO increases with the number of nodes which it has (51,52). The orbital ϕ_y has a node demanded by symmetry which automatically makes it H-H antibonding. On the other hand, ϕ_z has a node demanded by orthogonality conditions (with ϕ_s) which nearly passes directly through the oxygen nucleus. This latter node is thus present in a region of highest electron density and might be expected to impart a low I (high energy) to the MO. The other fact is that although ϕ_y is H-H antibonding, and

ϕ_z is H-H bonding, the former is expected to have relatively greater O-H bonding power. This is especially true for the observed bond angle of 105 degrees. The latter is, of course, the important factor, and would tend to give ϕ_y the lower energy (higher I).

In order to reconcile the fact that ionization from ϕ_y supposedly gives a Rydberg Series whereas ϕ_z does not, an analysis of the requirements for such a phenomenon should be made. A Rydberg Series, it is true, generally arises in the ionization of lone-pair electrons. The reason for this is that the ionized state is usually a stable one of approximately the same geometrical configuration as the ground state. Lone-pair electrons are not expected to be missed very much by a molecule. Thus, the prime requisite for a discrete set of transitions seems to be just these conditions. Now, one may consider the results to be expected from an ionization of a ϕ_y or a ϕ_z electron. If one electron from ϕ_y is ionized, there is a consequent loss of O-H bonding and H-H antibonding. The latter effect will tend to cause the H-O-H bond angle to become lessened. But with the loss of one ϕ_y electron, it is quite possible that the two ϕ_z electrons will be permitted to reorganize, that is, to move into the O-H bonding regions from which they were formerly excluded partially because of electrostatic repulsion. With the lessened H-O-H bond angle, the ϕ_z

electrons will be in a better position to give significant contribution to O-H, as well as H-H bonding. The superposed repulsion of the hydrogen nuclei will be expected to restrict the bond angle decrease to a minimum. It is thus quite possible that loss of a ϕ_y electron would result in a stable configuration differing little from that of the ground state.

If a ϕ_z electron is ionized, the proportion of H-H antibonding to bonding is increased. There seem to be no important factors present here to restrain the bond angle from considerably increasing. This could conceivably lead to an unstable ionized species. Consequently, a considerable number of discrete transitions leading to the ionized state, as is observed for the third I, would be unlikely.

It should finally be stressed that there is no real reason for contending that ϕ_z is very lone-pair like. It can be said that hybridization will lead to a weakening of the bonding in ϕ_z. This will result in more electron density on the back side of the oxygen than if hybridization had been neglected. The orbital will still be somewhat bonding and will still be predominently non-localized.

J. A. Pople (53) carried out a unique treatment of H_2O using as a basis the Lennard-Jones (54-57) method of equivalent orbitals (EO's). This approximation is an MO treatment. It depends upon the fact that an AP wave function

remains unchanged when subjected to a unitary transformation (1). There is such a transformation that will cause any AP to be such that each of its one-electron functions is by itself an eigenfunction of a Fock (modified Schrödinger) equation. These are generally denoted as MO's. Any other unitary transformation of this AP will give one-electron functions which are not eigenfunctions and which are called EO's. For H_2O, such a set might be made to roughly correspond to two lone pairs and two bonding EO's (neglecting 1s electrons).

Pople's treatment began with the general LCAO formulation of the MO's. Inner-shell-outer-shell mixing was neglected, only the 2s and 2p oxygen and 1s hydrogen AO's being explicitly considered. The lone-pair EO's were then secured by a unitary transformation of the MO's, a step which does not involve any loss of rigor. Three explicit approximations were then utilized in the formulation of the bond EO's: the orbitals were assumed to be localized; the oxygen hybrids in the EO's were assumed to be directed along the line of nuclei of the bonds; and the condition of orthogonality between bond EO's was simplified. A recent refinement of the method (58) has eliminated the last approximation. With these assumptions, the ordinary conditions of orthonormality of the EO's determine all but one of the LCAO coefficients. By introducing the empirical

value for the dipole moment, the EO's were determined. The initial calculation (53) included an approximation for one of the electric moment integrals, which was, however, rigorously evaluated in the most recent work (58).

The most significant result of this treatment is the fact that the lone-pair electrons are found to be chiefly responsible for the dipole moment of H_2O. This supports the results of the simple VB considerations by Coulson (17).

(b) The Principle of Maximum Overlap and the magic formula. In 1931, Slater (26) and Pauling (23) proposed as a rough measure of the strength of any covalent bond, formed by two electrons on adjacent atoms, the Principle of Maximum Overlap of the orbitals occupied by these electrons. This principle has been of great importance in the development of simple quantum mechanical analyses of chemical structures. Pauling and Sherman (45) found it convenient to call the magnitude of a bond orbital in its angular dependence the strength of the bond. Mulliken (59) and Maccoll (60) have independently proposed the more satisfying criterion of maximizing the radial and angular dependencies simultaneously. Recently, Mulliken (61) has given a more elegant quantitative form of this principle which he calls the magic formula.

The Principle of Maximum Overlap has been applied to

H_2O in only a very restricted sense. It has been indicated that to the first approximation the bond angle will be 90 degrees in order to secure the best overlap between 1s hydrogen AO's and pure 2p oxygen AO's. The two main factors that alter the situation, transfer of charge from the hydrogens to the oxygen and 2s-2p hybridization, have been generally only qualitatively stated.

The magic formula in its present form is to some degree limited by the fact that the corrections needed for resonance energy are still lacking. These are certainly required for a complete application to H_2O.

It has, nevertheless, seemed apropos to apply these two simple quantum chemical principles explicitly to H_2O. A study and comparison of the results should yield qualitative information regarding the electronic properties of H_2O as well as assist in evaluating the two methods.

The VB electron configuration for the covalent structure of H_2O may be written

$$1s)^2\phi_o)^2\phi_1.h')\phi_2.h'')2px)^2 \ . \qquad (2.29)$$

The functions ϕ_o, ϕ_1 and ϕ_2 are understood to be hybridized oxygen AO's (see page 15) based upon the second-order valence state (62)

$$0: \quad 1s)^2\phi_0)^2\phi_1)\phi_2)2px)^2, \; V_2 \; . \tag{2.30}$$

The hybrids may be formulated in the LCAO approximation as follows:

$$\begin{aligned}
\phi_o &= -(1 - 2c_{11}^2)^{\frac{1}{2}}2pz + 2^{\frac{1}{2}}c_{11}2s \\
\phi_1 &= c_{11}2pz + 2^{\frac{1}{2}}2py + 2^{-\frac{1}{2}}(1 - 2c_{11}^2)^{\frac{1}{2}}2s \\
\phi_2 &= c_{11}2pz - 2^{\frac{1}{2}}2py + 2^{-\frac{1}{2}}(1 - 2c_{11}^2)^{\frac{1}{2}}2s \; .
\end{aligned} \tag{2.31}$$

The coordinates used here are the same as described on page 26. Positive overlap is given by h' with 2pz and 2py. The LCAO hybridization coefficients have but one degree of freedom, manifested in c_{11}, since all other parameters are restrained by orthonormality and symmetry conditions.

It should be emphasized that consideration is being made here only of the covalent structure of H_2O corresponding to the state Ω_a of equation (2.12).

The maximization with respect to the parameter c_{11} of the overlap between h' and ϕ_1 is equivalent to that between h" and ϕ_2 by symmetry, and is conditioned by the equation

$$\begin{aligned}
dS(h',\phi_1)/dc_{11} &= S(h',2pz) \\
-2^{\frac{1}{2}}c_{11}(1 - 2c_{11}^2)^{-\frac{1}{2}} \; S(h',2s) &= 0.
\end{aligned} \tag{2.32}$$

The orbital 2pz may be resolved into a combination of 2pσ and 2pπ AO's relative to the O-H bond according to the equation:

$$2pz = 2p\sigma \sin w - 2p\pi \cos w \ , \qquad (2.33)$$

where w is the angle between O-H' and the y-axis. Since $S(h',2p\pi) = 0$, equation (2.32) can be solved to give

$$c_{11} = 2^{-\frac{1}{2}}(1 + F^2 \sin^2 w)^{-\frac{1}{2}} F \sin w \ , \qquad (2.34)$$

where $F = S(h',2p\sigma)/S(h',2s)$.

Incidentally, it is proven that the extremum defined by equation (2.32) is a maximum, since

$$d^2S(h',\phi_1)/dc_{11}^2 = -2^{1/2}(1 - 2c_{11}^2)^{-3/2}S(h',2s) < 0 \qquad (2.35)$$

if $c_{11} < 2^{-\frac{1}{2}}$.

For convenience, the hybrids given in equation (2.31) are relabeled as follows:

$$\begin{aligned} \phi_o &= c_{01}2pz + c_{02}2s \\ \phi_1 &= c_{11}2pz + 2^{-\frac{1}{2}}2py + c_{12}2s \\ \phi_2 &= c_{11}2pz - 2^{-\frac{1}{2}}2py + c_{12}2s \ . \end{aligned} \qquad (2.36)$$

The results determined from equation (2.34) for three values of the H-O-H angle are given in Table 2. The calculations were carried out utilizing orthogonalized Slater orbitals (63) with the usual effective nuclear charges: $Z(2s) = Z(2p) = 4.55$; and $Z(h) = 1$.

Table 2. Application of the Principle of Maximum Overlap to H_2O

H-O-H bond angle (degrees)	c_{01}	c_{02}	c_{11}	c_{12}	$S(h',\phi_1)$	$S(h',\phi_2)$
90	-0.90	0.45	0.32	0.63	0.56	0.21
105	-0.92	0.39	0.28	0.65	0.57_6	0.19
120	-0.94	0.33	0.24	0.67	0.58_4	0.16

It is first of all interesting to note that if the bond hybrids ϕ_1 and ϕ_2 were directed straight towards the hydrogens to which they are bonded, the coefficient c_{11} would have the values 0.71, 0.54 and 0.41 for 90, 105 and 120 degrees, respectively. Therefore, the hybrids are bent outwards beyond the O-H bonds. The required orthogonality between ϕ_1 and ϕ_2, combined with the fact that a large degree of 2s character is required for good overlap, is probably the cause of this result. In actuality, one

might expect a situation whereby the bonds are bent inwards, so as to provide a higher concentration of charge within the molecular triangle.

Upon cursory examination, the results also indicate the surprising conclusion that a bond angle greater than 120 degrees seems to be favored. This conclusion is reached by assuming that better bonding is attained only when overlap is increased. Hydrogen-hydrogen interaction, which in this VB representation would be an exchange repulsion, has not yet been included.

It can be shown that the overlap between the hydrogen 1s AO's and the lone-pair hybrid ϕ_o is equal to zero for all angles. The maximization has, therefore, extracted all possible overlap and concentrated it in the bonding hybrids. This treatment has, therefore, not taken proper cognizance of Pauling's supposition (24, p. 87) that the tendency to use best bond orbitals is resisted in the case of atoms with an unshared pair, since the latter incline to remain as more stable 2s AO's. This brings to light the chief objection to the present application. The lone-pair electrons have not been restrained in any way from being highly promoted from their stable 2s state. The gain in bonding energy by maximizing bond overlap, which apparently is equivalent to minimization of non-bonding overlap, would undoubtedly be largely lost by the energetic promotion of

the 2s electrons.

It might thus be concluded here that the Principle of Maximum Overlap in its rudimentary form should be maintained only as a most qualitative principle. It is to be anticipated that hybridization leading to increased bond overlap, and consequently, decreased non-bond overlap, is always working in competition with the promotion energy required to achieve such a valence condition. The usual rough concept of chemical bond formation consists essentially of two steps: (i) an excitation of the atoms to hybridized valence states, a process which requires energy; and (ii) the bringing together of the atoms, a process which leads to a lowering of the energy. This lowering is emphasized if the bond overlaps are increased (the Principle of Maximum Overlap). However, increasing the overlap by hybridization requires energy. A happy medium might be a maximization of the bond energy as a function of bond overlap minus the promotion energy required for the process of hybridization.

For the covalent VB configuration of H_2O as given in equation (2.29), the magic formula (61) for the dissociation energy D_o takes the form:

$$D_o = 2X(h',\phi_1) - 2Y(h',\phi_0) - Y(h',\phi_2) - 2Y(h',1s) \\ -Y(h',h'') + 2K(h',2px) - P + RE \ . \qquad (2.37)$$

The first term on the right hand side corresponds to the bond exchange energy and the next five terms to non-bonding exchange interactions. The seventh term denotes the promotion energy and RE refers to resonance energy.

To determine the promotion energy P, the antisymmetrized wave function for one spin-orbit configuration of the second-order valence state V_2' (62) of oxygen, defined in terms of the hybrids of equation (2.31), is written in determinantal form. There are four such determinantal wave functions, a linear combination of which defines the valence state V_2'. The individual functions correspond to all possible assignments of spin to the two bonding orbitals ϕ_1 and ϕ_2. The four configurations will thus be degenerate and non-interacting in this approximation, and it is sufficient to consider P for only one spin-orbital configuration determinant. The latter is expanded according to the rules for determinants into a linear combination of AP's in first-order hybridization. It can be shown that

$$\Phi(V_2') = 2^{\frac{1}{2}} c_{11} \Phi(k^2 s^2 p^4, V_2) + (1 - 2c_{11}^2)^{\frac{1}{2}} \Phi(k^2 sp^5, V_2) , \tag{2.38}$$

where k, s and p are the conventional abbreviations for 1s, 2s and 2p, respectively. Therefore,

$$E(V_2') = 2c_{11}^2\, E(k^2s^2p^4, V_2) + (1 - 2c_{11}^2)\, E(k^2sp^5, V_2) , \tag{2.39}$$

and

$$P = E(V_2') - E(k^2s^2p^4, {}^3P) = P_o + (1 - 2c_{11}^2)\,\Delta P , \tag{2.40}$$

where

$$P_o = E(k^2s^2p^4, V_2) - E(k^2s^2p^4, {}^3P) \tag{2.41}$$

and

$$\Delta P = E(k^2sp^5, V_2) - E(k^2s^2p^4, V_2) . \tag{2.42}$$

The actual computation of the various terms of equation (2.37) is accomplished using formulas given in reference (61). These formulas involve two parameters determined by fitting empirically the magic formula to the molecules CH, O_2, N_2 and F_2. The X's and Y's are then functions of the overlap integrals between the various orbitals as well as of suitable mean value valence state I's. The K is small and computed theoretically.

The first three terms of equation (2.37), as well as the promotion energy P, are functions of the hybridization parameter c_{11}. Therefore, the part of D_o containing these

terms, call it D', is maximized with respect to c_{11} for the H-O-H bond angles of 90, 105 and 120 degrees. The results are given in Table 3. It is seen that, for all practical purposes, the best hybridization is independent of bond angle in this region of angles. There is a slight tendency toward a lesser value of c_{11} as the bond angle increases. This corresponds to a greater 2s-2pz promotion in the lone-pair hybrid ϕ_o, which results in relatively higher 2py/2pz character in the bonding orbitals. The latter is, of course, to be favored as the bond angle increases.

For comparison with Table 2, the overlap integrals derived from the magic formula are listed in Table 4. The hybridization coefficients used are those from the 105 degree computation, namely,

$$\begin{aligned} c_{01} &= -0.410 \quad c_{11} = 0.645 \\ c_{02} &= 0.912 \quad c_{12} = 0.290 \ . \end{aligned} \tag{2.43}$$

It is interesting, at this point, to compare the results with those from the maximum overlap treatment.

It is seen that the degree of 2s promotion in ϕ_o is much less than for the maximum overlap treatment. The coefficient c_{11} is such that ϕ_1 and ϕ_2 are directly aligned towards h' and h", respectively, for a bond angle of about 95 degrees (see page 42). For bond angles greater than

Table 3. Maximization of D' with respect to hybridization (a.u.)

Terms of eq. (2.37)	H-O-H bond angle (degrees)	c_{11} 0.60	0.64	0.645	0.65	0.7071
	90	0.4993	0.4816	0.4787	0.4757	0.3832
$2X(h',\phi_1)$	105	0.4998	0.4812	0.4782	0.4751	0.3808
	120		0.4769	0.4738	0.4704	
	90	0.0871	0.1222	0.1275	0.1329	0.2542
$2Y(h',\phi_1)$	105	0.0983	0.1329	0.1379	0.1432	0.2542
	120		0.1452	0.1499	0.1550	
	90	0.0131	0.0091	0.0085	0.0080	0
$Y(h',\phi_2)$	105	0.0071	0.0041	0.0037	0.0033	0
	120		0.0011	0.0009	0.0007	
$(1 - 2c_{11}^2)\Delta P$		0.1697	0.1096	0.1018	0.0940	0
	90	0.2294	0.2407	0.2408	0.2409	0.1290
D'	105	0.2245	0.2346	0.2347	0.2346	0.1255
	120		0.2209	0.2211	0.2207	

this, the hybrids are bent inwardly as one might expect.

From the magnitudes of the overlap integrals, as well as of the corresponding energy terms in Table 3, it is seen that there must be considerable repulsion between the hydrogen valence shells and the inner ϕ_o lone pair. This point

Table 4. Overlap integrals for H_2O from the magic formula

H-O-H bond angle (degrees)	$S(h',\phi_o)$	$S(h',\phi_1)$	$S(h',\phi_2)$
90	0.3503	0.4759	0.1280
100	0.3595	0.4760	0.0991
105	0.3643	0.4751	0.0848
110	0.3693	0.4735	0.0705
120	0.3798	0.4686	0.0425

is relevant to the inner-shell-outer-shell repulsion encountered in molecule formation which is discussed extensively by Pitzer (64). The maximum overlap treatment gave $S(h',\phi_o)$ equal to zero. The repulsion between a hydrogen valence shell and the oxygen hybrid of the other bond, given by $Y(h',\phi_2)$, is seen to be quite negligible except for smaller bond angles.

In Table 5 are listed the resulting D_o values obtained be adding in the fourth to seventh terms of equation (2.37) to D'. It is seen that there is a definite maximum in the dissociation energy (minimum molecular energy) at a bond

Table 5. Computed D_o values from the magic formula

H-O-H bond angle (degrees)	D' (a.u.)	-Y(h',h") (a.u.)	Z[a] (a.u.)	D_o (a.u.)	D_o (e.v.)
90	0.2409	-0.0400	0.0311[b]	0.2320	6.31
100	0.2376	-0.0318		0.2369	6.45
105	0.2347	-0.0285		0.2373	6.46
110	0.2308	-0.0256		0.2363	6.43
120	0.2211	-0.0211		0.2311	6.28

a. $Z = -Y(h',1s) + 2K(h',\phi_3) - P_o$

$= -0.0015 + 2(0.0286) - 0.0246$ (a.u.).

b. Values are the same for all bond angles.

angle slightly less than 105 degrees. Mulliken obtains an average difference per electron pair bond between observed and computed D_o values of about ± 0.3 electron volts.

The RE correction for H_2O is expected to be considerable. No simple methods are presently capable of treating this problem. The position of the energy minimums for the

structures Ω_c and Ω_d of equation (2.13) would certainly be nearly or actually equal to 180 degrees. Depending, of course, upon the interaction at the various angles, one would expect such resonance to lead to a greater equilibrium angle for the resonating hybrid.

C. SCF MO Treatments of Other Molecules

1. Introduction

All of the treatments of H_2O which have been reviewed thus far have been carried out according to what Mulliken (65) has termed qualitative and semi-empirical methods. Roothaan's LCAO SCF MO theory (1), on the other hand, is referred to as an approximate theoretical method, that is, one which is purely theoretical, but uses approximate MO eigenfunctions of the LCAO type. Rather than here describe the method in detail, it is adequate to refer either to Mulligan's brief review of the subject (66) or to the original works (1,6,67).

2. Applications

The early approximate theoretical molecular treatments were necessarily and naturally confined to simple systems. For example, C. A. Coulson (68,69) carried out

extensive studies of H_2 and H_2^+, comparing the LCAO treatments with more sophisticated methods as well as studying the effect of varying the screening constants (effective nuclear charges) contained in the AO's. Also, Coulson and Duncanson (70) studied the LCAO approximation as applied to HeH^+ and HeH^{++}, again making comparisons of the results with more exact variational procedures, as well as with an exact treatment for the latter molecule. In 1943, these same researchers (71) carried out LCAO MO treatments of Li_2 in several approximations. This work is especially valuable for its discussion on screening constants and the effect of neglecting MO orthogonality.

Utilizing the Hückel π-electron approximation (72) for aromatic molecules, Goeppert-Mayer and Sklar (73) carried out the six-electron non-empirical treatment of the excited states of benzene. This calculation essentially uses LCAO SCF wave functions, and was responsible for much of the theoretical progress which has been made with respect to the unsaturated hydrocarbons. Inasmuch as numerical errors were present in this work, and three-center integrals were neglected, the treatment (without CI) has undergone final correction by Roothaan and Parr (74). The benzene problem has also been investigated with respect to variation of the effective nuclear charge of the carbon 2pπ AO (75). Crawford and Parr (76) utilized the method

in calculating the ring twisting constants for benzene. The π-electron approximation in its SCF MO form has been applied also to butadiene by Parr and Mulliken (77), to ethylene by Crawford and Parr (78), to allene by Parr and Taylor (79), and to acetylene by Ross (80). For ethylene and allene, vibrational frequencies were also computed, and for acetylene, the validity of the Hückel approximation was examined.

In recent years, the trend has been to investigate the success of the SCF MO method as applied to heteromolecules. Mulligan carried out a complete 22-electron treatment of CO_2 (66). Although approximations for many of the integrals were necessary, and no inner-shell-outer-shell mixing was allowed, the work may be regarded as quite successful.

I. Fischer (81) has carried out a very complete LCAO MO treatment of LiH. The results are compared with various VB approximations, as well as simplified versions of the MO method. Other recent SCF treatments which deserve mention are those by Fischer on aniline (82), by Duncan on SF_6 (83) and by Berthier on fulvene (84). These latter three cases utilize the Goeppert-Mayer and Sklar (73) effective core hamiltonian method for the potential due to inner non-valence electrons.

III. THE LCAO MO SELF-CONSISTENT FIELD TREATMENT OF H_2O

A. Application

1. General

The initial aim of the present calculation was to determine the best LCAO MO's for the ten electrons of the ground state of H_2O. The general method followed was that developed by Roothaan (1). All of the electrons were assigned to MO's extending throughout the molecule. In addition to this complete treatment, a second calculation was performed which contained the conventional approximation of replacing the innermost molecular shell by an oxygen 1s Slater orbital, and which considered no 1s-mixing in the outer shells.

(a) The selection of AO's. In these calculations, the following Slater functions (63) were utilized:

for the oxygen atom,

$$\begin{aligned} 1s = 0 &= \mu_1^{3/2}\pi^{-1/2} \exp(-\mu_1 r_o) \\ 2s' = s' &= \mu_2^{5/2}(3\pi)^{-1/2} r_o \exp(-\mu_2 r_o) \\ 2pz = z &= \mu_2^{5/2}\pi^{-1/2} r_o \cos\theta_o \exp(-\mu_2 r_o) \end{aligned} \qquad (3.1)$$

$$2px = x = \mu_2^{5/2}\pi^{-1/2}\, r_o \sin\theta_o \cos\phi_o \exp(-\mu_2 r_o)$$
$$2py = y = u_2^{5/2}\pi^{-1/2}\, r_o \sin\theta_o \sin\phi_o \exp(-\mu_2 r_o)\ ; \qquad (3.1)$$

and, for the hydrogen atoms,

$$ls_{h'} = h' = \mu^{3/2}\pi^{-1/2} \exp(-\mu\, r_{h'})$$
$$ls_{h''} = h'' = \mu^{3/2}\pi^{-1/2} \exp(-\mu\, r_{h''})\ . \qquad (3.2)$$

In general, μ_p is equal to Z_p/n_p, where Z_p is referred to as the effective nuclear charge, and n_p is the principle quantum number of the AO.

The attainment of best possible LCAO MO's depends upon the selection of the AO's. In the past, Slater-type AO's with the ordinary Slater Z's (63) have been most commonly used. Also, best Z-values for the free atoms are often utilized. It is to be expected, and there is evidence to this effect (6,68,81,85), that better results might be secured by independent variation of the Z's, even among identical AO's in different MO's. Such a procedure would, of course, entail very much additional work. Therefore, in this research, the following Slater μ-values were used:

$$\mu = 1$$
$$\mu_1 = 7.7 \qquad (3.3)$$
$$\mu_2 = 2.275$$

These are in reasonable agreement with the values which give the best analytical approximations of the Hartree-Fock atomic orbitals (86), namely,

$$\begin{aligned} \mu &= 1 \\ \mu_1 &= 7.68 \\ \mu_2 &= 2.22 \ . \end{aligned} \qquad (3.4)$$

All of the oxygen AO's given in (3.1) are mutually orthogonal with the exception of 1s and 2s'. Neglect of such orthogonality can cause serious errors in the simple Hartree method which does not utilize an AP wave function (34,68). No such error would occur in the present work, although the results would be changed somewhat. For consistency in formulation, it is convenient to preserve orthogonality between AO's on the same atom. Orthogonal 2s AO's were constructed from the original nodeless 2s' and 1s oxygen AO's (46):

$$2s = s = (1 - Q^2)^{-\frac{1}{2}} (2s' - Q1s) \ , \qquad (3.5)$$

where Q is the overlap integral between the 1s and 2s' AO's.

(b) Coordinates and internuclear distances. The coordinate systems used in these calculations are diagramed in Figure 1. The x-axis (not shown), is perpendicular to the plane of the molecule. The arrows indicate the

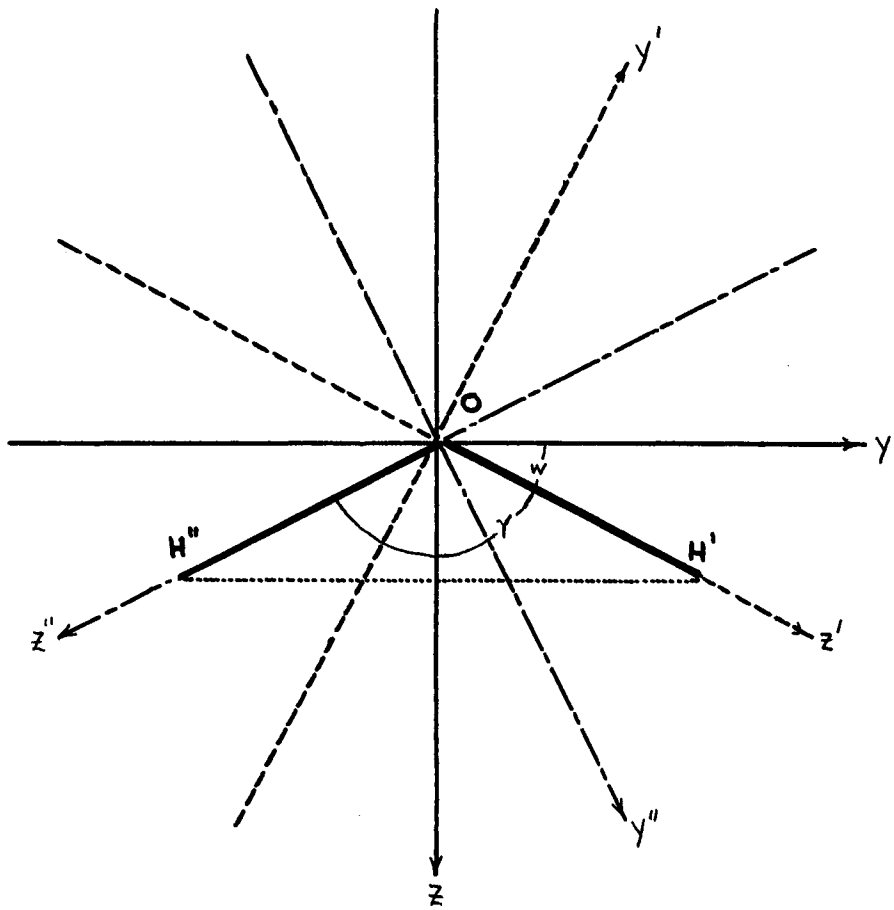

Figure 1. Coordinates used for the H_2O calculations

positive direction of the axes.

The transformations relating these coordinate systems may be written as follows:

$$
\begin{aligned}
z &= z'\sin w - y'\cos w = z''\sin w + y''\cos w \\
y &= z'\cos w + y'\sin w = -z''\cos w + y''\sin w \\
\\
y' &= y\sin w - z\cos w = -z''\sin 2w - y''\cos 2w \\
z' &= y\cos w + z\sin w = -z''\cos 2w + y''\sin 2w \\
\\
y'' &= y\sin w + z\cos w = -y'\cos 2w + z'\sin 2w \\
z'' &= -y\cos w + z\sin w = -y'\sin 2w - z'\cos 2w
\end{aligned}
\qquad (3.6)
$$

It is to be noted that the 2p oxygen AO's based upon the various coordinate systems transform according to these equations (46). The 2p AO's oriented in the various directions will often be designated according to these axes in a manner illustrated as follows:

$$
\begin{aligned}
2pz &= z \\
2py' &= y' \\
2pz'' &= z'' \ .
\end{aligned}
\qquad (3.7)
$$

In these calculations, the experimentally observed O-H distance, 0.9581 angstroms (42) or 1.8103 atomic units, was used throughout. The SCF calculations were carried out for six different values of the H-O-H bond angle: 90, 100, 105, 110, 120 and 180 degrees.

(c) The formation of SO's. In order to obtain proper symmetry for the MO's, it is usually convenient to introduce symmetry orbitals (SO's) (1). These are linear combinations of AO's taken so as to belong to irreducible representations of the symmetry group of the molecule. The H_2O molecule belongs to the symmetry group C_{2v} (87).

The construction of the SO's from the AO's may be expressed in matrix form as follows:

$$\begin{bmatrix} \sigma_1' \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5' \\ \sigma_6 \\ \sigma_7 \end{bmatrix} = \begin{bmatrix} 2^{-\frac{1}{2}} & 0 & 0 & 0 & 2^{-\frac{1}{2}} & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 2^{-\frac{1}{2}} & 0 & 0 & 0 & -2^{-\frac{1}{2}} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} h' \\ o \\ s \\ z \\ h'' \\ y \\ x \end{bmatrix} \qquad (3.8)$$

The first four SO's have A_1 symmetry, σ_5 and σ_6 have B_2 and σ_7 has B_1 symmetry. It is to be noted that the SO's involving the equivalent hydrogen AO's are not normalized. The corresponding normalized SO's are

$$\begin{aligned} \sigma_1 &= 2^{-\frac{1}{2}}N_1(h' + h'') = 2^{-\frac{1}{2}}[1 + S(h',h'')]^{-\frac{1}{2}}(h' + h'') \\ \sigma_5 &= 2^{-\frac{1}{2}}N_5(h' - h'') = 2^{-\frac{1}{2}}[1 - S(h',h'')]^{-\frac{1}{2}}(h' - h'') , \end{aligned} \qquad (3.9)$$

where S(h',h") denotes the overlap integral between the two hydrogen AO's.

(d) The formation of the MO's. By taking linear combinations of SO's possessing the same symmetry, a like number of MO's having that symmetry are formed. The latter are given in matrix form as follows:

$$\begin{bmatrix} \phi(1a_1) \\ \phi(2a_1) \\ \phi(3a_1) \\ \phi(4a_1) \\ \phi(1b_2) \\ \phi(2b_2) \\ \phi(1b_1) \end{bmatrix} = \begin{bmatrix} c_{11} & c_{12} & c_{13} & c_{14} & 0 & 0 & 0 \\ c_{21} & c_{22} & c_{23} & c_{24} & 0 & 0 & 0 \\ c_{31} & c_{32} & c_{33} & c_{34} & 0 & 0 & 0 \\ c_{41} & c_{42} & c_{43} & c_{44} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{55} & c_{56} & 0 \\ 0 & 0 & 0 & 0 & c_{65} & c_{66} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & c_{77} \end{bmatrix} \begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \\ \sigma_7 \end{bmatrix} . \qquad (3.10)$$

The MO's are denoted by the symbol of the irreducible representation to which they belong, preceded by a running number distinguishing orbitals of identical symmetry.

The coefficients in the MO's which are occupied (by two electrons) in the ground state AP will be designated by the general symbol c_{ip}. For H_2O, these occupied MO's are $\phi(1a_1)$, $\phi(2a_1)$, $\phi(3a_1)$, $\phi(1b_2)$ and $\phi(1b_1)$. The SCF procedure also yields the coefficients and eigenvalues for the unoccupied orbitals $\phi(4a_1)$ and $\phi(2b_2)$. These will not

be of immediate concern in these calculations, but will be pertinent to later discussion concerning excited states.

The problem will be the determination of the coefficients c_{ip}. These could be referred to as linear-combination-of-symmetry-orbitals (LCSO) coefficients. Inasmuch as they are related directly to the AO's by (3.8), they will be called by the more common name, LCAO coefficients.

2. Determination of the best LCAO MO's

The ground state electronic energy of H_2O in the MO approximation (without CI) is given by equation (2.4), in which Γ_f is replaced by Φ_o (see page 9). In the LCAO approximation, Φ_o is the AP of those MO's given in equations (3.10) which are considered to be filled in the lowest energy electronic configuration.

To determine the SCF orbitals, it is necessary to solve the equations

$$\underline{F}\ \underline{c_i} = \underline{\epsilon_i}\ \underline{S}\ \underline{c_i} \ . \qquad (3.11)$$

An equation of this type becomes identical with an ordinary eigenvalue problem of a hermitian matrix if $\underline{S}$ is replaced by the unit matrix. The detailed development of this equation is given by Roothaan (1). A brief derivation is outlined in Mulligan's paper on CO_2 (66). In equation (3.11),

F may be regarded as the total electronic energy matrix, and is equal to the sum of the bare nuclear field energy matrix H and the total electronic interaction matrix G. The c_i are column vectors, the elements of which are the c_{ip} given in (3.10).

All of the calculations were carried out using the non-normalized SO's as given in equations (3.8). Therefore, all of the equations and tables will be given in terms of these orbitals with the exception of the final SCF MO results (e.g. Table 16).

(a) The S-matrix. The elements of the S-matrix are very simply given in terms of overlap integrals involving SO's; that is,

$$S_{pq} = \int \bar{\sigma}_p^{\mu} \, \sigma_q^{\mu} \, dv^{\mu}, \qquad (3.12)$$

where p and q denote the row and column, respectively. These are computed from the appropriate overlap integrals over AO's (see Tables 9 and 10). The final values for the various bond angles are given in Table 6.

(b) The H-matrix. This matrix includes the kinetic energy of the electrons and their potential energy in the field of the three nuclei. The elements are given by

$$H_{pq} = \int \bar{\sigma}_p^{\mu} \, H^{\mu} \, \sigma_q^{\mu} \, dv^{\mu}, \qquad (3.13)$$

Table 6. Non-zero elements (S_{pq}) of the S-matrices

p q	H-O-H bond angle (degrees)					
	90	100	105	110	120	180
1 1	1.4440	1.3958	1.3746	1.3553	1.3223	1.2406
1 2	0.0862[a]					
1 3	0.6994[a]					
1 4	0.3479	0.3163	0.2995	0.2822	0.2460	0
2 2	1.0000[a]					
3 3	1.0000[a]					
4 4	1.0000[a]					
5 5	0.5560	0.6042	0.6254	0.6447	0.6777	0.7594
5 6	0.3479	0.3769	0.3903	0.4030	0.4261	0.4920
6 6	1.0000[a]					
7 7	1.0000[a]					

a. Values are the same for all bond angles.

where

$$H^{\mu} = -\tfrac{1}{2}\Delta^{\mu} - (1/r^{h'\mu}) - (1/r^{h''\mu}) - (8/r^{o\mu}) \ . \quad (3.14)$$

The numerical values for the H-matrix elements are given in Table 7. These have been computed from the appropriate kinetic energy integrals over AO's (see Tables 8, 9, 10) and bare nuclear field repulsion integrals over SO's (see Table 15).

(c) The G-matrix. The terms of this matrix present the most difficulty. They represent the interaction of an electron in the MO ϕ_i with all of the other electrons of the molecule. Each element is a rather complicated function of all of the LCAO coefficients c_{ip}, which are initially unknown. Therefore, once given a set of assumed c_{ip}'s, it is convenient to have a fast method for computation of the G_{pq}'s. Mulligan (6) has devised such a procedure, which will be followed here.

The elements may be written in general as follows (1,66):

$$G_{pq} = \sum_{i} \sum_{r} \sum_{s} c_{ir} \, G_{prqs} \, c_{is} \ , \quad (3.15)$$

where

$$G_{prqs} = 2J_{prqs} - J_{prsq} \quad (3.16)$$

Table 7. Elements (H_{pq}) of the H-matrices (a.u.)

p q	H-O-H bond angle (degrees)					
	90	100	105	110	120	180
1 1	-7.4982	-7.2235	-7.1025	-6.9927	-6.8034	-6.3572
1 2	-2.7533	-2.7528	-2.7527	-2.7526	-2.7523	-2.7516
1 3	-5.1431	-5.1303	-5.1233	-5.1162	-5.1063	-5.0724
1 4	-2.4395	-2.2147	-2.0957	-1.9755	-1.7242	0
2 2	-33.0598[a]					
2 3	-0.3165[a]					
2 4	-0.0233	-0.0212	-0.0201	-0.0189	-0.0165	0
3 3	-8.1120[a]					
3 4	-0.2579	-0.2345	-0.2221	-0.2092	-0.1824	0
4 4	-7.6443	-7.6229	-7.6123	-7.6021	-7.5825	-7.5207
5 5	-2.4398	-2.6606	-2.7586	-2.8480	-3.0030	-3.3668
5 6	-2.2500	-2.4434	-2.5346	-2.6187	-2.7736	-3.2258
6 6	-7.6443	-7.6658	-7.6763	-7.6866	-7.7061	-7.7679
7 7	-7.5207[a]					

a. Values are the same for all bond angles.

and

$$J_{prqs} = (pq:rs) = \int \bar{\sigma}_p^{\mu}\ \bar{\sigma}_r^{\nu}\ (1/r_{\mu\nu})\ \sigma_q^{\mu}\ \sigma_s^{\nu}\ dv_{\mu\nu} \quad . \tag{3.17}$$

The summation over i is taken over all MO's of the closed-shell ground state. The summations over r and s are determined by the non-zero coefficients contained in the various LCAO MO's.

When equation (3.15) is expanded in general terms, the result can be written

$$G_{pq} = \sum_{n=1}^{14} d_n\ D_{pq}^{(n)} \quad . \tag{3.18}$$

The $D_{pq}^{(n)}$'s are linear combinations of integrals of the type (3.17). These sums may be written in general as follows:

$$\begin{aligned}
D_{pq}^{(1)} &= 2(pq:11) - (p1;q1) \\
D_{pq}^{(2)} &= 2(pq:22) - (p2:q2) \\
D_{pq}^{(3)} &= 2(pq:33) - (p3:q3) \\
D_{pq}^{(4)} &= 2(pq:44) - (p4:q4) \\
D_{pq}^{(5)} &= 4(pq:12) - (p1:q2) - (p2:q1) \\
D_{pq}^{(6)} &= 4(pq:13) - (p1:q3) - (p3:q1) \\
D_{pq}^{(7)} &= 4(pq:14) - (p1:q4) - (p4:q1) \\
D_{pq}^{(8)} &= 4(pq:23) - (p2:q3) - (p3:q2) \\
D_{pq}^{(9)} &= 4(pq:24) - (p2:q4) - (p4:q2)
\end{aligned} \tag{3.19}$$

$$
\begin{aligned}
D_{pq}^{(10)} &= 4(pq:43) - (p4:q3) - (p3:q4) \\
D_{pq}^{(11)} &= 2(pq:55) - (p5:q5) \\
D_{pq}^{(12)} &= 2(pq:66) - (p6:q6) \\
D_{pq}^{(13)} &= 4(pq:56) - (p5:q6) - (p6:q5) \\
D_{pq}^{(14)} &= 2(pq:77) - (p7:q7) \,.
\end{aligned}
\tag{3.19}
$$

The d_n's are functions of the ground state LCAO coefficients c_{ip}, and have the following forms:

$$
\begin{aligned}
d_1 &= c_{11}^2 + c_{21}^2 + c_{31}^2 \\
d_2 &= c_{12}^2 + c_{22}^2 + c_{32}^2 \\
d_3 &= c_{13}^2 + c_{23}^2 + c_{33}^2 \\
d_4 &= c_{14}^2 + c_{24}^2 + c_{34}^2 \\
d_5 &= c_{11}c_{12} + c_{21}c_{22} + c_{31}c_{32} \\
d_6 &= c_{11}c_{13} + c_{21}c_{23} + c_{31}c_{33} \\
d_7 &= c_{14}c_{11} + c_{24}c_{21} + c_{34}c_{31} \\
d_8 &= c_{12}c_{13} + c_{22}c_{23} + c_{32}c_{33} \\
d_9 &= c_{12}c_{14} + c_{22}c_{24} + c_{32}c_{34} \\
d_{10} &= c_{13}c_{14} + c_{23}c_{24} + c_{33}c_{34} \\
d_{11} &= c_{55}^2 \\
d_{12} &= c_{56}^2 \\
d_{13} &= c_{55}c_{56} \\
d_{14} &= c_{77}^2 = 1 \,.
\end{aligned}
\tag{3.20}
$$

The D_{pq}'s corresponding to each matrix element as a

function of bond angle were computed from the electronic repulsion integrals over SO's (see Table 14). These remained the same throughout the complete SCF calculation. For a given set of c_{ip}'s, the d_n's were then computed and the summation (3.18) was carried out.

(d) The SCF procedure. The solution of equations (3.11) reduces to the determination of the roots ϵ_i of the determinant

$$\begin{aligned} |\underline{F} - \underline{\epsilon}\,\underline{S}| &= 0 \\ \text{or} \qquad |\underline{H} + \underline{G} - \underline{\epsilon}\,\underline{S}| &= 0 \,. \end{aligned} \tag{3.21}$$

Since the matrix elements are evaluated in terms of symmetry orbitals, it can be shown (1) that the determinant (3.21) is considerably simplified. For the H_2O problem, (3.21) was reduced to one four-by-four, one two-by-two and one one-by-one determinants.

A reasonable set of coefficients c_{ip} were chosen, $\underline{G}$ and hence $\underline{F}$ were calculated, and the five lowest roots of (3.21) were determined by the method of James and Coolidge (3). This method also yields the corresponding coefficients c_{ip}, which are solutions of (3.11). The latter were compared with the assumed values, and generally found to be different. The process was then repeated until self-consistency was attained.

It was found that the fastest procedure is to utilize the computed c_{ip}'s as the assumed coefficients for the succeeding SCF trial. The solutions of (3.21) are automatically orthogonal and are normalized. The divergencies arising from not using strictly orthonormal trial functions are probably relatively large. The mechanical construction of an orthonormal set is a tedious process. Therefore, considerable time was saved by continuously feeding the resulting coefficients back into the secular equations.

B. Evaluation of Integrals

1. General

The AO's utilized in the evaluation of all integrals are those defined in equations (3.1) and (3.2). Results are tabulated for integrals involving both nodeless and orthogonalized 2s AO's. All values are given in the Hartree atomic units (defined in footnote on page 4), except, of course, overlap integrals, which are dimensionless. The various types of integrals involving AO's are designated in the tables by the following symbols:

overlap integrals,

$$S(\chi_p, \chi_q) = \int \bar{\chi}_p^{\mu} \chi_q^{\mu} \, dv^{\mu} \; ; \qquad (3.22)$$

kinetic energy integrals,

$$(\chi_p T \chi_q) = \int \chi_p^{\mu} \left(-\tfrac{1}{2}\Delta^{\mu}\right) \chi_q^{\mu} \, dv^{\mu} \; ; \qquad (3.23)$$

nuclear-field attraction integrals,

$$(A: \chi_p \chi_q) = \int \chi_p^{\mu} \left(1/r^{\mu A}\right) \chi_q^{\mu} \, dv^{\mu} \; ; \qquad (3.24)$$

and electronic repulsion integrals,

$$(\chi_p \chi_q : \chi_r \chi_s) = \int \chi_p^{\mu} \chi_q^{\mu} \left(1/r^{\mu\nu}\right) \chi_r^{\nu} \chi_s^{\nu} \, dv^{\mu} \, dv^{\nu} . \qquad (3.25)$$

The integrals are classified as one-, two-and three-center integrals depending upon the number of functional origins involved. Examples of each are, respectively, (hTh), (O:oh) and (h'h":h's).

2. One- and two-center integrals involving AO's

The values for all one-center integrals are listed in Table 8. In Table 9, the results are tabulated for all two-center integrals involving only the two 1s hydrogen AO's. The values for these integrals depend, of course, upon the H-O-H bond angle. In Table 10 are given all two-center integrals which involve oxygen AO's. These are evaluated using the convention that the positive z'-axis passes through the primed hydrogen (see Figure 1, page 57).

All of the one- and two-center integrals either were

Table 8. One-center integrals over AO's

Integral	Value (a.u.)	Ref.	Integral	Value (a.u.)	Ref.
S(os')	0.23345	a,b,c	(oo:ss)	1.1334	b
(h'Th')	0.5000	a	(oo:zz)	1.1297	b
(oTo)	29.6450	a,b	(os:os)	0.0703	a,b
(oTs)	-8.0885	a	(os:ss)	-0.0181	a
(sTs)	3.0869	b	(os:zz)	-0.0097	a
(zTz)	2.5878	b	(oz:oz)	0.0265	b
(H':h'h')	1.0000	a	(oz:sz)	0.0349	a
(0:oo)	7.7000	a,b	(ss:ss)	0.8039	b
(0:os)	-1.0505	a	(ss:zz)	0.8137	b
(0:ss)	1.2636	b	(sz:sz)	0.1750	b
(0:zz)	1.1375	b	(zz:zz)	0.8905	b
(h'h':h'h')	0.6250	a	(zz:yy)	0.7945	b
(oo:oo)	4.8125	a,b	(zy:zy)	0.0480	b
(oo:os)	-0.4498	a			

a. Calculated using analytical expressions given by C. C. J. Roothaan (88).

b. Values obtained from tables given by J. F. Mulligan (66).

c. Value checked with R. S. Mulliken *et al.* (46).

Table 9. Two-center integrals over AO's involving only hydrogen AO's (a.u.)

Integral	H-O-H bond angle (degrees)						Ref.
	90	100	105	110	120	180	
S(h'h")	0.44403	0.39576	0.37459	0.35531	0.32234	0.24064	a,b
(h'Th")	0.05315	0.03777	0.03174	0.02661	0.01867	0.00336	a
(H':h"h")	0.3823	0.3553	0.3438	0.3336	0.3165	0.2753	a
(H':h'h")	0.2752	0.2357	0.2190	0.2043	0.1798	0.1237	a
(h'h':h"h")	0.3621	0.3407	0.3313	0.3228	0.3082	0.2715	a
(h'h":h'h")	0.09947	0.0770	0.06849	0.06104	0.04938	0.02621	c
(h'h':h'h")	0.2169	0.1880	0.1757	0.1643	0.1461	0.1025	d,e

a. Calculated using analytical expressions given by C. C. J. Roothaan (88).

b. Values checked with R. S. Mulliken et al. (46).

c. Interpolated from tables of J. O. Hirschfelder and J. W. Linnett (89).

d. Calculated from independently derived expressions.

e. Checked with tables of J. O. Hirschfelder and J. W. Linnett (89).

Table 10. Two-center integrals over AO's involving oxygen AO's

Integral	Value (a.u.)	Ref.	Integral	Value (a.u.)	Ref.
S(h'o)	0.06098	a,b	(H':sz')	0.1824	d
S(h's')	0.5088	a,b,c	(H':z'z')	0.6279	a,c
S(h's)	0.4946	d	(H':y'y')	0.5043	a,c
S(h'z')	0.3479	a,b,c	(O:h'h')	0.5108	a,c
(h'To)	0.0045	a	(H':oh')	0.0350	a
(h'Ts')	0.1315	a	(H':s'h')	0.3859	a,c
(h'Ts)	0.1342	d	(H':sh')	0.3885	d
(h'Tz')	0.2375	a	(H':z'h')	0.4114	a,c
(H':oo)	0.5524	a	(O:oh')	0.2353	a
(H':os')	0.1289	a	(O:s'h')	0.4365	a,c
(H':os)	-0.0005	d	(O:sh')	0.3924	d
(H':oz')	0.0165	a	(O:z'h')	0.2501	a,c
(H':s's')	0.5455	a,c	(h'h':oo)	0.5099	a
(H':ss)	0.5451	d	(h'h':os')	0.1184	a
(H':s'z')	0.1812	a,c	(h'h':os)	-0.00069	d

a. Calculated using analytical expressions given by C. C. J. Roothaan (88).

b. Value checked with R. S. Mulliken et al. (46).

c. Compared with values obtained from M. Kotani et al. (90).

d. Derived from appropriate integrals involving nodeless 2s AO's.

Table 10. (Continued)

Integral	Value (a.u.)	Ref.	Integral	Value (a.u.)	Ref.
(h'h':oz')	0.0112	a	(h's':h's')	0.1748	g
(h'h':s's')	0.4806	a,c	(h's:h's)	0.1725	d
(h'h':ss)	0.4792	d	(h's':h'z')	0.1349	g
(h'h':s'z')	0.1075	a,c	(h's:h'z')	0.1339	d
(h'h':sz')	0.1078	d	(h'z':h'z')	0.1331	g
(h'h':z'z')	0.5103	a,c	(h'y':h'y')	0.02845	g
(h'h':y'y')	0.4658	a,c	(h'h':h'o)	0.0318	h
(h'o:h'o)	0.00903	e	(h'h':h's')	0.2864	c,h
(h'o:h's')	0.0275	f	(h'h':h's)	0.2789	d
(h'o:h's)	0.0261	d	(h'h':h'z')	0.2599	c,h
(h'o:h'z')	0.0202	f	(h'o:oo)	0.1917	h

a. Calculated using analytical expressions given by C. C. J. Roothaan (88).

c. Compared with values obtained from M. Kotani *et al.* (90).

d. Derived from appropriate integrals involving nodeless 2s AO's.

e. Calculated accurately to five decimal places by the method of Rudenberg (91).

f. Approximated; see pages 98-100.

g. Interpolated (Lagrangian) from tables of M. Kotani *et al.* (90).

h. Calculated from independently derived expressions.

Table 10. (Continued)

Integral	Value (a.u.)	Ref.	Integral	Value (a.u.)	Ref.
(h'o:os')	0.0333	h	(h's':z'z')	0.3578	c,i
(h'o:os)	-0.0114	d	(h's:z'z')	0.3525	d
(h'o:oz')	0.0013	i	(h's':s's')	0.3530	c,h
(h'o:s's')	0.0649	h	(h's:ss)	0.3425	d
(h'o:ss)	0.0632	d	(h's':s'z')	0.04613	c,i
(h'o:s'z')	0.0025	i	(h's:sz)	0.0466	d
(h'o:sz')	0.0022	d	(h's':y'y')	0.3454	c,i
(h'o:z'z')	0.0643	i	(h's:y'y')	0.3400	d
(h'o:y'y')	0.0635	i	(h'z':oo)	0.2498	h
(h's':oo)	0.4341	h	(h'z':os')	0.0578	h
(h's:oo)	0.4005	d	(h'z':os)	-0.0005	d
(h's':os')	0.1025	h	(h'z':oz')	0.0154	i
(h's:os)	0.0038	d	(h'z':s's')	0.2207	c,h
(h's':oz')	0.0065	i	(h'z':ss)	0.2073	d
(h's:oz')	0.0062	d	(h'z':s'z')	0.0949	c,i

c. Compared with values obtained from M. Kotani *et al.* (90).

d. Derived from appropriate integrals involving nodeless 2s AO's.

h. Calculated from independently derived expressions.

i. Calculated using analytical expressions given by M. P. Barnett and C. A. Coulson (92).

Table 10. (Continued)

Integral	Value (a.u.)	Ref.	Integral	Value (a.u.)	Ref.
(h'z:sz')	0.0939	d	(h'y':s'y')	0.0661	c,i
(h'z':z'z')	0.2361	c,i	(h'y':sy')	0.0651	d
(h'z':y'y')	0.2083	c,i	(h'y':z'y')	0.0104	c,i
(h'y':oy')	0.0119	h			

c. Compared with values obtained from M. Kotani et al. (90).

d. Derived from appropriate integrals involving nodeless 2s AO's.

h. Calculated from independently derived expressions.

i. Calculated using analytical expressions given by M. P. Barnett and C. A. Coulson (92).

obtained from existing tables or were computed by standard methods indicated in the references. It will be noticed that in many cases, independent checks upon the values were obtained.

Many of the one-center integrals were taken from tables published by Mulligan (66). It should be noted that Mulligan's published values are twice those quoted here, since his unit of energy was one-half of that utilized in these calculations.

3. Exact methods for three-center integrals involving AO's

Relatively simple exact evaluation of three-center integrals may be carried out in those special cases in which all AO's involved have the same effective nuclear charge and the centers lie on a straight line. Such cases have been considered by Hirschfelder and co-workers (93,94), whose work is based on that of Schuchowitzky (95) and Gordadse(96). These types do not occur in the H_2O calculations.

Coulson (97) has described a method for certain three-center cases which has recently been utilized (98) as a general basis for two-center integral calculations. The principle of the method is the infinite series expansion of an AO on one center in terms of products of spherical harmonics and bessel functions on a second center.

Many-center integrals are thus reduced to one- or two-center integrals in this manner. This type of expansion was utilized in the present calculations for the evaluation of the three-center nuclear attraction integral (0:h'h"). The details of this computation are furnished in Appendix A.

Other methods based upon the expansion of an AO on one center in terms of spherical harmonics on another center have been described by several workers, notably Coolidge (18), Landshoff (99) and Lundqvist and Löwdin (100). Recently, Rüdenberg (101) has described a method which is quite similar in nature to the above treatments. It involves the expansion of an AO in terms of a complete orthogonal set of AO's on another center. This method was investigated quite extensively during the course of these calculations. Two three-center integrals were treated numerically, but the series involved were not carried to complete convergence. These two integrals may, therefore, be considered to be quite reliably approximated. Details of the method and calculation are given in Appendix B.

Barker and Eyring (102) have recently reported a general formulation of the three-center nuclear attraction integral. The treatment has only been outlined specifically for s-type AO's. The method is based upon the Neumann expansion of 1/r in terms of the fixed elliptical coordinates of the attracting center and of the ordinary

elliptical coordinates of the electron. In this sense, it is probably closely related to Rüdenberg's method (91) for two-center exchange integrals. The work was published after the SCF problem had been completed and, therefore, could not be utilized in this connection.

4. Approximate methods for three-center integrals involving AO's

There are 32 three-center integrals involved in the SCF energy calculations on H_2O. It is well recognized that their neglect can lead to very serious errors (74,75,78, 103,104,105). Therefore, in many theoretical calculations, it has been considered a wise policy to include all many-center integrals even though rough approximations have had to be utilized. Exact computation of three-center integrals is, indeed, a difficult task due to the fact that in most cases their solutions cannot be written in closed form. Until machine-computed tables are constructed in order to simplify the calculations, it will usually be necessary to rely upon approximate methods.

It has been one of the primary aims of this treatment to secure the best possible approximate values for all three-center integrals without expending an unreasonable amount of time. For most MO treatments which have required

approximate values for integrals, the simple point-charge (66), the Mulliken (6,67) or the Sklar (106) approximations have been used in the past.

All of the three-center integrals are functions of the H-O-H bond angle, which will be denoted by the symbol γ hereafter. In general, R without a subscript will refer to the observed O-H distance.

Table 11 lists the values for all of the three-center integrals. Inasmuch as each was treated as an individual problem, the approximations are discussed in the following paragraphs.

(a) The semi-point-charge-approximation (SPCA) and (h'h":h'o). Because of the large Z-value associated with the 1s oxygen AO, the charge distribution h'o is practically a point-charge. Replacing one continuous charge distribution contained in a two-electron repulsion integral by a point-charge will be called an SPCA. The amount of charge represented by h'o is given by its overlap integral. Therefore, the SPCA for this integral may be written

$$(h'h'':h'o) \simeq S(h',o)(0:h'h'') \; . \qquad (3.26)$$

For γ equal to zero degrees, (h'h":h'o) equals (h'h':h'o), a two-center integral, the exact value of which is

Table 11. Three-center integrals involving AO's (a.u.)[a]

Integral	Paragraph[b]	H-O-H bond angle (degrees)					
		90	100	105	110	120	180
(O:h'h")	(a)	0.2540	0.2310	0.2207	0.2113	0.1949	0.1564
(h'h":s's')	(a)	0.2389	0.2189	0.2104	0.2027	0.1897	0.1532
(h'h":z'z')	(a)	0.2419	0.2211	0.2125	0.2049	0.1923	0.1577
(h'h":h'o)	(a)	0.0155	0.0141	0.0135	0.0129	0.0119	0.0095
(H":h'o)	(b)	0.0337	0.0334	0.0333	0.0332	0.0330	0.0325
(h"h":h'o)	(c)	0.0315	0.0314	0.0314	0.0313	0.0313	0.0312
(h'h":h's')	(d)	0.1292	0.1175	0.1123	0.1075	0.0992	0.0796
(H":h's')	(e)	0.244	0.236	0.231	0.226	0.219	0.196
(H":h's)	(e)	0.243	0.234	0.229	0.224	0.217	0.193
(h"h":h's')	(f)	0.2237	0.2146	0.2116	0.2089	0.2045	0.1920
(h"h":h's)	(f)	0.2225	0.2132	0.2101	0.2073	0.2028	0.1910

a. Inasmuch as all values given here are approximate, except for (O:h'h"), the number of figures given are not necessarily "significant figures".

b. Letters refer to paragraph headings in Chapter III, B, 4.

Table 11. (Continued)

Integral	Paragraph[a]	H-O-H bond angle (degrees)					
		90	100	105	110	120	180
(h'h":h'z)	(g)	0.0625	0.0517	0.0467	0.0422	0.0339	0
(h'h":h'y)	(g)	0.0625	0.0616	0.0609	0.0602	0.0587	0.0544
(H":h'z')	(h)	0.1701	0.1557	0.1494	0.1436	0.1335	0.1065
(H":h'y)	(h)	0.0533	0.0620	0.0670	0.0705	0.0780	0.1065
(H":h'z)	(h)	0.1873	0.1683	0.1581	0.1497	0.1319	0
(h"h":h'z)	(i)	0.1600	0.1460	0.1400	0.1320	0.1160	0
(h"h":h'y)	(i)	0.0550	0.0650	0.0700	0.0740	0.0810	0.1110
(h"o:h'o)	(j)	0.00895	0.00894	0.00894	0.00893	0.00892	0.00887
(h"o:h's')	(k)	0.0266	0.0265	0.0264	0.0263	0.0262	0.0257
(h"o:h's)	(k)	0.0252	0.0251	0.0250	0.0249	0.0248	0.0243
(h"o:h'z')	(l)	0.0155	0.0145	0.0141	0.0136	0.0128	0.0101
(h"o:h'y')	(l)	-0.0033	-0.0028	-0.0025	-0.0022	-0.0016	0
(h"o:h'z)	(l)	0.0133	0.0115	0.0106	0.0096	0.0078	0

a. Letters refer to paragraph headings in Chapter III, B, 4.

Table 11. (Continued)

Integral	Paragraph[a]	H-O-H bond angle (degrees)					
		90	100	105	110	120	180
(h"o:h'y)	(l)	0.0086	0.0093	0.0097	0.0099	0.0103	0.0101
(h"s':h's')	(m)	0.1540	0.1520	0.1500	0.1490	0.1470	0.1330
(h"s:h's)	(m)	0.1509	0.1489	0.1468	0.1458	0.1437	0.1292
(h"s':h'z)	(n)	0.0849	0.0760	0.0716	0.0670	0.0579	0
(h"s':h'y)	(n)	0.0680	0.0729	0.0752	0.0773	0.0812	0.0925
(h"s:h'z)	(n)	0.0841	0.0754	0.0711	0.0666	0.0577	0
(h"s:h'y)	(n)	0.0679	0.0727	0.0750	0.0771	0.0810	0.0927
(h"z:h'z)	(o)	0.074	0.065	0.062	0.058	0.051	0.010
(h"y:h'y)[b]	(o)	-0.0337	-0.0393	-0.0421	-0.0448	-0.0499	-0.0660
(h"y:h'y)[c]	(o)	-0.005	-0.011	-0.014	-0.016	-0.022	-0.038

a. Letters refer to paragraph headings in Chapter III, B, 4.

b. Mulliken approximation.

c. Modified Mulliken approximation; see paragraph (o).

Table 11. (Continued)

Integral	Paragraph[a]	H-O-H bond angle (degrees)					
		90	100	105	110	120	180
(h"x:h'x)	(p)	0.0193	0.0182	0.0178	0.0172	0.0162	0.0100
(h"z:h'y)	(q)	0.0323	0.0315	0.0307	0.0298	0.0272	0
(h'h":oz)	(t)	0.0030	0.0025	0.0022	0.0020	0.0015	0
(h'h":ss)	(u)	0.2381	0.2181	0.2098	0.2022	0.1894	0.1530
(h'h":xx)	(v)	0.2301	0.2107	0.2025	0.1952	0.1828	0.1502
(h'h":yy)	(v)	0.239	0.219	0.211	0.204	0.192	0.158
(h'h":zz)	(v)	0.241	0.221	0.211	0.203	0.190	0.150

a. Letters refer to paragraph headings in Chapter III, B, 4.

0.0318 atomic units. The SPCA gave the value 0.0312. One expects the SPCA to be low here since there is an excess of interpenetration of h'h' and oh' which is not accounted for by the approximation.

In general, an SPCA of the repulsion between two spherically symmetric distributions will be high. If the distribution which is replaced by the point-charge is polarized towards the other distribution, the SPCA will be closer to or lower than the exact value. It is often possible to determine the sign of the error of an SPCA by judicious analysis.

For Υ's equal to and approaching 180 degrees, one might expect this approximation to be very poor due to the rather extensive immersion of the oh' distribution in the cylindrically symmetric h'h" function. In this respect, it is interesting to compare the values obtained from the exact computation of (0:h'h") and the rather reliable approximations of (h'h":s's') and (h'h":z'z') (see Table 11, p. 80). It is seen that, although for large Υ the distributions become quite intermixed, the SPCA still appears to be a rather reliable approximation.

The resulting approximations of (h'h":h'o) according to (3.26) are given in Table 11, page 80.

(b) (H":h'o) and the charged sphere approximation. Recently, R. G. Parr (107) has given a method for

estimating electronic repulsion integrals over LCAO MO's involving Slater 2pπ AO's. This treatment includes an approximation in which the electronic charge distributions are replaced by uniformly charged spheres of finite size. This approximation has been extended in the present calculations to enable the estimation of a variety of integrals involving AO's.

The h'o distribution was replaced by a uniformly charged sphere of total charge Q equal to S(h',o). The radius R_1 of the sphere was fixed by the equation

$$(h'o:h'o) = 0.00903 \simeq 6Q^2/(5R_1) , \qquad (3.27)$$

whereby R_1 equals 0.494 atomic units. This charged sphere approximation was found by deriving the classical energy of repulsion between two superimposed uniformly charged spheres of equal diameter (see Appendix C). The fact that the h'o distribution is not actually spherically symmetric, but polarized towards h', was accounted for by placing the charged sphere at a distance R_o from O towards H'. R_o was determined by the approximation

$$(H':h'o) = 0.0350 = Q/(R - R_o) , \qquad (3.28)$$

where R is the O-H distance. R_o is found to be 0.068 atomic units.

For the general three-center integral (H":oh'), the

charged sphere approximation takes the form

$$(H'':oh') = Q/R_1', \quad R_1' > R_1 \tag{3.29}$$

where

$$R_1' = (R^2 + R_o^2 + 2RR_o \cos 2w)^{\frac{1}{2}} . \tag{3.30}$$

The results are given in Table 11, page 80.

It should be noted that the point-charge approximation of (H":oh') should be reasonably valid, especially for large γ. For γ equal to 180 degrees, the result is Q/R or 0.034 atomic units. This is expected to be high since the real center of the oh' distribution is polarized away from H". In the charged sphere approximation, this was accounted for by displacement of the sphere from O. A similar displacement introduced into the point-charge model makes the methods identical in this special case. For more complicated integrals, this degeneracy will not occur.

In anticipation of more general charged sphere approximations, there is gathered in Appendix C a number of formulae giving the energies of repulsion between such spheres for various specific cases.

(c) The integral (h"h":h'o) and an inequality rule for hybrid integrals. This integral has the value 0.0318 atomic units for γ equal to zero degrees. The SPCA gave the value 0.0312 atomic units for all γ. The true value of the

integral for γ equal to 180 degrees would be expected to be less than 0.0312.

The charged sphere approximation was applied to this integral by replacing the h"h" distribution by a uniformly charged sphere of radius

$$\begin{aligned} R_h &\simeq (1.2)/(hh{:}hh) \\ &= (1.2)/(0.625) \\ &= 1.92 \text{ atomic units.} \end{aligned} \qquad (3.31)$$

This relation was derived using equation (C.5) in Appendix C. The oh' distribution was replaced by a point-charge of magnitude s(o,h') at a distance R_o of 0.068 atomic units from O along OH'. Then, using equation (C.6),

$$(h"h":h'o) \simeq Q(3R_h^2 - R'^2)/(2R_h^3) , \qquad (3.32)$$

where R' is the distance between the center of the h"h" sphere and the point-charge. At γ equal to zero degrees, this approximation gave 0.0346 atomic units, and at 180 degrees, 0.0324 atomic units. It was then assumed that the per cent error in this approximation is the same for all γ. This assumption is probably quite valid, since the position of the charge moves only 0.136 atomic units in a sphere of radius 1.92 atomic units as γ goes from zero to 180 degrees. The value obtained for γ equal to zero degrees was 0.0318 atomic units (the exact value fixed by assuming a constant

8.8 per cent error) and 0.0298 for γ equal to 180 degrees.

This charged sphere approximation of (h"h":h'o) was not carried out until after the SCF calculations were completed. The value 0.0312 was utilized at 180 degrees, and a linear interpolation between zero and 180 degrees was taken to obtain the intermediate values listed in Table 11, page 80.

One may now develop a useful inequality between the values for (h"h":h'o) and (H":h'o), or, in general, for $(ls_a ls_a : \chi_b \chi_c)$ and $(A : \chi_b \chi_c)$, where χ_b and χ_c are any two AO's on two different centers. By integrating over the coordinates of the electron represented by $ls_a ls_a$, it may be shown that

$$(ls_a ls_a : \chi_b \chi_c) = (A : \chi_b \chi_c) - \pi \mu_a^{-3} \left[(A : ls_a ls_a \chi_b \chi_c) + \mu_a S(ls_a ls_a \chi_b \chi_c) \right] . \tag{3.33}$$

The first integral on the right-hand side of this equation is generally more easily approximated than the electronic repulsion integral. It is not always obvious which is the larger. The signs of the second two integrals on the right-hand side of the equation may often be found by inspection and thus determine an inequality. For example, (H:h"h"oh') and S(h"h"oh') are always greater than zero since their integrands are positive in all space.

Therefore, (h"h":h'o) is less than (H":h'o). This inequality might be expected to become less pronounced as γ increases. This is seen to be true of the results given in Table 11, page 80.

(d) The integral (h'h":h's). The SPCA was utilized for approximating this integral. The resulting values for both the nodeless and orthogonalized 2s AO's are given in Table 11, page 80.

(e) The integral (H":h's). The h's' distribution was replaced by a point-charge of magnitude S(h',s') at the point of maximum overlap along the O-H' internuclear axis. For γ equal to 180 degrees, this point-charge approximation may be written as follows:

$$\begin{aligned}(H":h's') &\simeq S(h's')/(R + 0.785) \\ &= 0.196 \text{ atomic units.}\end{aligned} \qquad (3.34)$$

The charged sphere approximation was applied in the same manner as it was for (H":h'o). The result is 0.193 atomic units for γ equal to 180 degrees.

A rough graph was drawn connecting the exact value at zero degrees and the assumed value of 0.196 atomic units at 180 degrees. The results are given in Table 11, page 80.

(f) The integral (h"h":h's). The SPCA of (h"h":h's') for γ equal to 180 degrees was applied by placing a

point-charge of magnitude S(h',s') at the maximum in the overlap of h's' along the O-H' axis. The result is 0.192.

The Mulliken approximation (6) of this integral may be formulated as follows:

$$(h''h'':h's') \approx \tfrac{1}{2} S(h',s') \left[(h'h':h''h'') + (h''h'':s's')\right] . \tag{3.35}$$

This gives the value 0.2813 at γ equal to zero (the exact value is 0.2864) and 0.192 at 180 degrees. The intermediate results as given by this approximation (slightly modified to give the correct result at zero degrees) are listed in Table 11, page 80.

(g) The integrals (h'h'':h'y) and (h'h'':h'z). These two integrals were computed by the SPCA. The results are given in Table 11, page 81.

The Mulliken approximation shows general agreement with the above method with regard to the general variation with γ. The difference between the two never exceeds 0.014 atomic units, the Mulliken method being the lower at all except very small γ.

(h) (H'':h'z) and (H'':h'y). These two integrals are probably the most difficult to estimate accurately. It is believed that the charged sphere approximation is the most reliable of the approximations used for these cases.

The integral (H":h'z') was initially considered. This can be related to the above integrals by the transformations indicated in equations (3.6). The distribution h'z' was replaced by a pair of tangent uniformly charged spheres of radii R_1 and R_2, and charges $Q_1(<0)$ and $Q_2(>0)$, respectively. The following formulas were obtained by using equations in Appendix C:

$$\begin{aligned}
(h'z':h'z') &\simeq 2Q_1Q_2/(R_1 + R_2) + 6Q_1^2/5R_1 + 6Q_2^2/5R_2 ; \\
(H':h'z') &\simeq Q_2/(R_1 - R_2) + Q_1/(R + R_1), \; R_2 < R/2 ; \\
(0:h'z') &\simeq Q_2/R_2 + Q_1/R_1 ;
\end{aligned} \tag{3.36}$$

and

$$S(h',z') \simeq Q_1 + Q_2 .$$

For γ equal to 180 degrees,

$$(H":h'z') \simeq Q_2/(R + R_2) + Q_1/(R - R_1) , \; R_1 < R/2 . \tag{3.37}$$

The right-hand sides of these five equations contain four unknowns: Q_1, Q_2, R_1 and R_2. If one takes R_1 and R_2 equal to the distances from 0 to the appropriate maxima of h'z' measured along the internuclear axis (0.306 and 0.785 atomic units), one can use the fourth equation and one of the first three equations to determine Q_1 and Q_2. Approximations can then be obtained for the other three integrals. Table 12 gives the results of these calculations.

It is seen from the first three calculations that

(H":h'z') is rather insensitive to the choice of equations used to determine the parameters. The significance of $|Q_1| + Q_2$ is especially interesting. This corresponds to the integrated absolute overlap between h' and z'; the

Table 12. Application of the charged sphere approximation

Integral	Exact value	Calculated approximate values			
		1	2	3	4
(h'z':h'z')	0.1331	(0.1331)			
(H':h'z')	0.4114	0.369	0.388	(0.4114)	
(H":h'z')	------	0.117	0.107	0.092	0
(0:h'z')	0.2501	0.323	(0.2501)	0.15	
$\|Q_1\| + Q_2$		0.469	0.540	0.642	1.30

value should be in the vicinity of 0.509, which is the overlap between h' and s'. It is seen that the value of zero given to (H":h'z') yields an absurd value for $|Q_1| + Q_2$.

It was assumed that $|Q_1| + Q_2$ is equal to 0.509, a reasonable value for this quantity. Then, Q_1 equals -0.0806 and Q_2 equals 0.4284. The second and third equations (3.36) were solved simultaneously for R_1 and R_2, giving 0.322 and 0.827 atomic units, respectively. These

values of the parameters should give good values for (H":h'z') for all γ. The results are given in Table 11, page 81.

The integral (H":h'y) is equivalent to (H":h'z') for γ equal to 180 degrees. From the above approximation, it is, therefore, equal to 0.107 at this γ. The exact value of (H":h'y) at zero degrees is zero. A roughly linear curve was plotted between these extremes.

The integral (H":h'z) is determined by utilizing the above approximations of (H":h'y) and (H":h'z') and applying the transformation equations given in (3.6). The final values for (H":h'z) and (H":h'y) are given in Table 11, page 81.

(i) <u>The integrals (h"h":h'z) and (h"h":h'y)</u>. The inequality condition which was described in connection with (h"h":h'o) may be applied to these two integrals. It can be shown that the following relations are correct:

$$(h"h":h'z) < (H":h'z)$$

and (3.38)

$$(h"h":h'y) > (H":h'y) .$$

The charged sphere approximation was applied to (h"h":h'z') for zero and 180 degrees, which are equivalent to (h"h":h'z) at zero degrees and (h"h":h'y) at 180 degrees,

respectively. The spheres used for h"h" and h'z' were the same as those used for (h"h":h'o) and (H":h'z'), respectively. For γ equal to zero degrees, the charged sphere approximation gives the formula

$$Q_1/(R + R_1) + Q_2[15R_h^2 - 3R_2^2 - 5(R - R_2)^2]/(10R_h^3) = 0.256, \qquad (3.39)$$

and for 180 degrees,

$$Q_2/(R + R_2) + Q_1[15R_h^2 - 3R_1^2 - 5(R - R_1)^2]/(10R_h^3) = 0.111. \qquad (3.40)$$

The value 0.256 atomic units is in good agreement with the exact value, 0.2599, and 0.111 for γ equal to 180 degrees agrees well with the inequality cited in equation (3.38).

The final values for the integrals (h"h":h'z) and (h"h":h'y) are listed in Table 11, page 81.

(j) The integral (h'o:h"o) and a modified Sklar approximation. A method was developed for the approximation of exchange integrals of the type $(1s_a \chi_b : \chi_c \chi_d)$ in which $\mu(1s_a)$ is small and $\mu(\chi_b)$ is large. The approximation is described here for the special case in which χ_b is an s-type AO.

Consider first the charge distribution $1s_a ns_b$. It may be written in analytical form as follows:

$$1s_a ns_b = N_a N_b r_b^{n-1} \exp(-\mu_a r_a - \mu_b r_b) , \qquad (3.41)$$

where N_a and N_b are normalization constants. The magnitude of the exponential part measured on the internuclear axis A-B may be expressed in simpler forms. Let the distance A-B be R and designate region I as that being to the left of A, region II as that being between A and B and region III to the right of B. Then,

$$\exp(-\mu_a r_a - \mu_b r_b) = \begin{cases} \exp(-\mu_b R) \exp(-\mu_a r_a - \mu_b r_a) & \text{I} \\ \exp(-\mu_a R) \exp(-\mu_b r_b + \mu_a r_b) & \text{II} \\ \exp(-\mu_a R) \exp(-\mu_b r_b - \mu_a r_b) & \text{III.} \end{cases} \qquad (3.42)$$

It is quite obvious that if $\mu(ns_b)$ is large and $\mu(1s_a)$ is small, the exponential part will be negligible except in regions II and III. In order to secure a single exponential which will be approximately applicable in either of these regions, the average of the exponents is taken to give

$$\exp(-\mu_a r_a - \mu_b r_b) \simeq \exp(-\mu_a R) \exp(-\mu_b r_b) . \qquad (3.43)$$

Therefore,

$$1s_a ns_b \simeq N_a N_b \exp(-\mu_a R) r_b^{n-1} \exp(-\mu_b r_b) . \qquad (3.44)$$

The two-center charge distribution has thus been approximated by a one-center distribution. One could utilize equation (3.44) directly for approximating integrals. However, it was found advantageous to fix the amount of charge in the approximated version so as to be equal to the exact overlap $S(1s_a,ns_b)$. The approximation then takes the form

$$1s_a ns_b \simeq S(1s_a,ns_b)1s_b' ns_b'/S(1s_b',ns_b') \ , \qquad (3.45)$$

where $\mu(1s_a') = \mu(ns_b') = \frac{1}{2}\mu(ns_b)$. The method now strongly resembles similar approximations used by Sklar (106). The mononuclear overlap integral may be formulated simply as follows:

$$S(1s_b',ns_b') = (n+1)!\,[(2n)!2]^{-\frac{1}{2}} \ . \qquad (3.46)$$

Some numerical results of this approximation as applied to the integral $(1s_a1s_b:1s_a1s_b)$, $\mu(1s_a) = 1$, are given in Table 13. In these cases, the charge distributions for electrons one and two were each approximated, yielding a mononuclear integral. Greater accuracy could probably be attained by approximating only one charge distribution in each integral, and computing the appropriate hybrid integral. It is seen from Table 13 that the approximation tends to give low results. If applied to a three-center integral $(1s_ans_b:1s_cns_b)$, the approximation is

independent of the angle A-B-C, inasmuch as the distributions are replaced by one-center s-type functions. Therefore, from the nature of the method, one might be inclined to consider the approximate result as a good mean value of

Table 13. Examples of the modified Sklar approximation

$\mu(1s_b)$	R (a.u.)	$(h_a1s_b:h_a1s_b)$	
		Approximate (a.u.)	Exact (a.u.)
2.69	2.64	0.0149	0.0158[a]
2.69	3.02	0.0075	0.0077[a]
2.69	3.40	0.0037	0.0037[a]
3.69	2.48	0.0106	0.0106[a]
7.7	1.8103	0.00895	0.00903

a. From tables given by Fischer (81).

the integral for all bond angles. It will, therefore, be generally assumed that the value is valid for a 90 degree bond angle.

For (h'o:h"o), a linear variation with respect to γ is assumed. The exact value at zero degrees, 0.00903 atomic units, and the approximate result at 90 degrees,

0.00895 (Table 13), are utilized to determine the variation.

(k) The integral (h'o:h"s) and the modified Mulliken approximation. The Mulliken approximation (6) of the integral (h'o:h'o) gives the result 0.0060 atomic units, which is 33.5 per cent too low. The same approximation applied to (h's':h's') is 0.1565, which is low by 10.5 per cent. On the basis of intuition alone, it might be expected that the Mulliken approximation of (h'o:h's') should be in error to some intermediate extent. Assuming an average error, 22.0 per cent, the Mulliken approximation of (h'o:h's'), 0.0213, is modified to give the value 0.0275.

The modified Sklar approximation may be applied to this integral as follows:

$$(h'o:h"s') \simeq S(h'o)(ls_o'ls_o':h's')/S(ls_o'ls_o') \quad , \quad (3.47)$$

where $\mu(ls_o') = \frac{1}{2}\mu(o) = 3.85$. This gives the result 0.0265, which is expected to be valid for a bond angle of 90 degrees (vide supra).

The SPCA was applied to this integral as follows:

$$(h'o:h's') \simeq S(h',o)(0:h's') = 0.0266. \quad (3.48)$$

This value is expected to be low due to the strong interpenetration of h'o and h's' not accounted for by the (O:h's') interaction. This same type of integral (with different values for R and the μ's) has been computed

exactly by Fischer (81). The exact value is given as 0.0179, whereas the SPCA gives 0.0168.

The values 0.0275 for γ equal to zero degrees, and 0.0266 at 90 degrees were assumed in order to obtain the final results given in Table 11, page 81.

(1) The integrals (h"o:h'z) and (h"o:h'y). These two integrals were transformed to (h"o:h'z') and (h"o:h'y') using equations (3.6). The latter integrals are more easily approximated.

The modified Sklar approximation gives the result 0.0152 atomic units for (h"o:h'z'). This value is expected to be a good approximation for γ equal to 90 degrees.

The SPCA applied to (h"o:h'z') gives the value 0.0153. Fischer's (81) exact values for this type of two-center integral may be compared to the corresponding SPCA's: 0.0262 (0.0228), 0.0171 (0.0153), 0.0123 (0.0100) and 0.0250 (0.0224), the approximations being enclosed in parentheses. The values are expected to be low as compared to the exact for γ equal to zero degrees. This approximation does not account for a strong interpenetration of the positive portion of h'z' and h'o, which gives a greater repulsion than accounted for by S(h'o)(0:h'z').

The charged sphere approximation was applied to (h"o:h'z'). The h"o distribution was treated in the same manner as for (h"h":h'o), and h'z the same as for (H":h'z').

The results of this method are given in Table 11, page 81. The value for γ equal to 90 degrees agrees well with the approximations discussed above.

The Mulliken approximation of (h'z':h'z') gives the value 0.0767, which is 42.3 per cent too low. For (h'o:h'o), the error is 33.5 per cent low. Assuming that this approximation is 37.9 per cent too low for (h'o:h'z'), the value 0.0238 is obtained, which is in quite good agreement with that obtained by the charged sphere approximation (0.0212).

The integral (h"o:h'y') was approximated by the charged sphere method for γ equal to 90 degrees. The h"o distribution was replaced in the same manner as for (h"h":h'o) and (h"o:h'z'). The h'y' charge distribution was approximated by two equal tangent spheres of opposite charge. The radii R_1 used were determined by utilizing the geometric mean of the two radii involved in the h'z' charged spheres. This turned out to be 0.525 atomic units. The charge Q to be associated with each sphere was determined by the relation

$$(h'y':h'y') = 0.0285 \simeq -Q^2/R_1 + 12Q^2/(5R_1) = 7Q^2/(5R_1) . \qquad (3.49)$$

If R_1 equals 0.525, Q is found to be 0.103. The total integrated overlap of h'y' would then be 2Q, or 0.206,

which is probably a reasonable value for this quantity.

The integral (h"o:h'y') is equal to zero by symmetry considerations for γ equal to zero and 180 degrees. For intermediate angles, the charged sphere results are given in Table 11, page 82. The slight maximum for γ equal to 120 degrees might be qualitatively explained by the fact that a decrease in repulsion is expected as h"o moves into the negative lobe of h'y (as γ approaches 180 degrees).

(m) The integral (h's:h"s). The Mulliken approximation of (h's':h's') is 0.1565 atomic units. The true value is 0.1748. It was assumed that the per cent error is a constant independent of γ. The resulting values are given in Table 11, page 82.

The charged sphere approximation was applied to this integral for γ equal to 180 degrees. The h's' distribution was derived in the same manner as for (H":h's'). The radius of the sphere, R_1, was found from the approximation

$$(h's':h's') = 0.1748 \simeq 6Q^2/(5R_1) , \qquad (3.50)$$

where Q equals S(h',s'). R_1 was thus determined to be 1.78 atomic units. The distance from O to the center of the sphere, R_o, was calculated by the approximation

$$(H':h's') = 0.3859 \simeq Q[3R_1^2 - (R - R_o)^2]/(2R_1) , \qquad (3.51)$$

in which it was found that R_o equals 0.829 atomic units. For γ equal to 180 degrees, (h's':h's') is represented by two equivalent uniformly charged spheres which intersect such that the distance between their centers is $2R_o$. Equation (C.2) may be used to determine the repulsion. The result, 0.133, is in exact agreement with the adjusted Mulliken approximation given in Table 11, page 82.

(n) The integrals (h"s:h'z) and (h"s:h'y). The Mulliken approximation of (h"s':h'z) is assumed to be 19.85 per cent low for all γ.

The same approximation is 42.3 and 10.5 per cent low for (h'z':h'z') and (h's':h's'), respectively. The modified Mulliken approximation would then indicate that (h"s':h'z') should be approximately 26.4 per cent too low. This might indicate that a geometric mean per cent error should be investigated in preference to the average per cent error originally recommended for the modified Mulliken approximation. This would give 20.2 per cent, which is in better agreement with the true error, 19.85 per cent.

The Mulliken approximation of (h"s':h'y) is used as such. By pictorially analyzing the interactions involved in this integral and (h"s:h'z) it may be shown that for a bond angle of 90 degrees, the value of the latter should exceed that of the former. This is because at this angle, h"s' is farther from the positive lobe of h'y than from

h'z, and also penetrates the negative lobe of h'y more than that of h'z.

(o) The integrals (h"z:h'z) and (h"y:h'y). The exact value of the first integral for γ equal to zero degrees is 0.1331 atomic units. The Mulliken approximation at this angle was found to be 42.3 per cent too low. At 180 degrees, this approximation gives a value of zero, which also is expected to be low. For this γ, the charged sphere approximation was applied as follows:

$$(h'z:h''z) = -2Q_1^2/(2R_o') + 12Q_1^2/(5R_1) - Q_1^2[80(2R_o)^2R_1^3 - 30(2R_o)^3R_1^2 + (2R_o)^5]/(80R_1^6) \quad (3.52)$$

The parameters used are those derived for (h"o:h'y'). R_o' is the distance from 0 to the center of any of the four spheres involved. The answer obtained was 0.0120 atomic units. Before this calculation had been performed, the value 0.0100 atomic units was derived by quite qualitative means. This was the value which was used. A linear variation of (h'z:h"z) with γ was assumed.

The results of the Mulliken approximation of (h"y:h'y) are given in Table 11, page 82. All of these values are probably too low, inasmuch as the true value for γ equal to

zero degrees is 0.0285 atomic units compared with the approximate result of zero.

The charged sphere approximation may be rigorously applied to (h"y:h'y) for γ equal to 180 degrees. The following expression was derived using equations from Appendix C:

$$(h'y:h''y) \simeq -Q_1^2/(2R_1) - Q_2^2/(2R_2) - 2Q_1Q_2[15R_2^2 - 3R_1^2 - 5(R_2 - R_1)^2]/(10R_2^3). \quad (3.53)$$

The values for all parameters were obtained from approximation number 1 of Table 12. The result of equation (3.53) was -0.0327 atomic units.

If one adds 0.0285 to the value given by the Mulliken approximation for γ equal to 180 degrees, the adjusted result of -0.0375 atomic units is obtained. This agreement with the charged sphere approximation seems to indicate that such an adjusted Mulliken approximation should be reasonable.

(p) The integral (h'x:h"x). The true value of this integral for γ equal to zero degrees is 0.0285. For γ equal to 180 degrees, the value 0.0100 from paragraph (o) is utilized.

(q) The integral (h"z:h'y). The Mulliken approximation of this integral is used for all values of γ.

(r) The integral (h'h":oo). The SPCA for this integral is utilized for all angles; that is,

$$(h'h'':oo) \approx (0:h'h''). \qquad (3.54)$$

For γ equal to zero, the error is about 0.2 per cent.

(s) The integral (h'h":os). The SPCA was assumed for the integral (h'h":os'). This led to the value of zero for (h'h":os) for all values of γ. The true value at zero degrees is -0.0007.

(t) The integral (h'h":oz). For γ equal to zero, the exact value is 0.0112, and at 180 degrees, the exact value is zero. A rough plot was constructed to obtain the intermediate values.

(u) The integral (h'h":ss). The integral (h'h":s's') was evaluated by the exact Rüdenberg method (Appendix B) without carrying the series to complete convergence.

(v) The integrals (h'h":xx), (h'h":zz) and (h'h":yy). The integral (h'h":z'z') was obtained to fair accuracy by the Rüdenberg method (Appendix B). These results, combined with the SPCA (see paragraph a) and some minor changes to

obtain a logical order in the values at γ equal to 180 degrees, are given in Table 11, page 83.

5. Evaluation of integrals involving symmetry orbitals

The integrals involving symmetry orbitals are easily expressed in terms of integrals over AO's by first utilizing the transformation given in (3.6) and then, if necessary, the transformations of equations (3.8). The resulting numerical values are tabulated for all bond angles in Tables 14 and 15.

Table 14. Electronic repulsion integrals over symmetry orbitals (a.u.)

Integral	H-O-H bond angle (degrees)					
	90	100	105	110	120	180
11:11	1.0267	0.9358	0.8980	0.8636	0.8082	0.6795
11:12	0.0666	0.0646	0.0637	0.0629	0.0614	0.0579
11:13	0.5373	0.5142	0.5046	0.4958	0.4808	0.4447
11:14	0.3315	0.2945	0.2769	0.2584	0.2219	0
11:22	0.7639	0.7409	0.7306	0.7212	0.7048	0.6663
11:23	-0.0007[a]					
11:24	0.0109	0.0097	0.0090	0.0084	0.0071	0
11:33	0.7173	0.6974	0.6890	0.6815	0.6686	0.6322
11:34	0.1038	0.0913	0.0851	0.0794	0.0674	0
11:44	0.7290	0.7052	0.6933	0.6834	0.6669	0.6160
11:55	0.3941	0.4058	0.4097	0.4129	0.4172	0.4220
11:56	0.2572	0.2774	0.2814	0.2880	0.2994	0.3392
11:66	0.7270	0.7109	0.7048	0.6996	0.6912	0.6683
11:77	0.6959	0.6765	0.6683	0.6610	0.6486	0.6160
12:12	0.0180	0.0180	0.0180	0.0180	0.0180	0.0179
12:13	0.0513	0.0512	0.0511	0.0510	0.0509	0.0504
12:14	0.0276	0.0245	0.0229	0.0212	0.0179	0
12:22	0.2711[a]					
12:23	-0.0162[a]					

a. Values are the same for all bond angles.

Table 14. (Continued)

Integral	H-O-H bond angle (degrees)					
	90	100	105	110	120	180
12:24	0.0013	0.0012	0.0011	0.0011	0.0009	0
12:33	0.0893[a]					
12:34	0.0022	0.0020	0.0019	0.0018	0.0016	0
12:44	0.0904	0.0903	0.0902	0.0902	0.0901	0.0898
12:55	0.0228	0.0247	0.0256	0.0264	0.0278	0.0311
12:56	0.0229	0.0248	0.0257	0.0264	0.0278	0.0303
12:66	0.0904	0.0905	0.0905	0.0906	0.0907	0.0910
12:77	0.0898[a]					
13:13	0.3234	0.3214	0.3193	0.3183	0.3162	0.3017
13:14	0.1788	0.1615	0.1526	0.1434	0.1247	0
13:22	0.5663[a]					
13:23	0.0054[a]					
13:24	0.0062	0.0056	0.0053	0.0050	0.0043	0
13:33	0.4843[a]					
13:34	0.0466	0.0424	0.0401	0.0378	0.0330	0
13:44	0.4897	0.4881	0.4874	0.4866	0.4852	0.4808
13:55	0.1719	0.1818	0.1870	0.1918	0.2005	0.2199
13:56	0.1626	0.1753	0.1812	0.1868	0.1970	0.2266
13:66	0.4897	0.4912	0.4920	0.4927	0.4941	0.4985
13:77	0.4808[a]					

a. Values are the same for all bond angles.

Table 14. (Continued)

Integral	H-O-H bond angle (degrees)					
	90	100	105	110	120	180
14:14	0.1548	0.1367	0.1292	0.1209	0.1056	0.0385
14:22	0.2498	0.2271	0.2151	0.2026	0.1766	0
14:23	-0.0005	-0.0005	-0.0004	-0.0004	-0.0004	0
14:24	0.0192	0.0188	0.0186	0.0184	0.0180	0.0168
14:33	0.2073	0.1885	0.1785	0.1682	0.1466	0
14:34	0.1120	0.1089	0.1072	0.1055	0.1023	0.0921
14:44	0.2326	0.2108	0.1994	0.1877	0.1632	0
14:55	0.1547	0.1482	0.1448	0.1391	0.1260	0
14:56	0.0846	0.0830	0.0812	0.0790	0.0725	0
14:66	0.2118	0.1931	0.1832	0.1728	0.1510	0
14:77	0.2083	0.1893	0.1793	0.1689	0.1473	0
22:22	4.8125[a]					
22:23	-0.4498[a]					
22:24	0[a]					
22:33	1.1334[a]					
22:34	0[a]					
22:44	1.1297[a]					
22:55	0.2559	0.2789	0.2892	0.2986	0.3150	0.3535
22:56	0.2498	0.2706	0.2803	0.2894	0.3059	0.3533
22:66	1.1297[a]					

a. Values are the same for all bond angles.

Table 14. (Continued)

Integral	H-O-H bond angle (degrees)					
	90	100	105	110	120	180
22:77	1.1297[a]					
23:23	0.0703[a]					
23:24	0[a]					
23:33	-0.0181[a]					
23:34	0[a]					
23:44	-0.0097[a]					
23:55	-0.0007[a]					
23:56	-0.0005	-0.0006	-0.0006	-0.0006	-0.0006	-0.0007
23:66	-0.0097[a]					
23:77	-0.0097[a]					
24:24	0.0264[a]					
24:33	0[a]					
24:34	0.0349[a]					
24:44	0[a]					
24:55	0.0049	0.0047	0.0046	0.0044	0.0041	0
24:56	0.0025	0.0025	0.0024	0.0023	0.0022	0
24:66	0[a]					
24:77	0[a]					
33:33	0.8039[a]					
33:34	0[a]					

a. Values are the same for all bond angles.

Table 14. (Continued)

Integral	H-O-H bond angle (degrees)					
	90	100	105	110	120	180
33:44	0.8136[a]					
33:55	0.2412	0.2611	0.2695	0.2770	0.2898	0.3262
33:56	0.2073	0.2246	0.2326	0.2402	0.2539	0.2932
33:66	0.8136[a]					
33:77	0.8136[a]					
34:34	0.1749[a]					
34:44	0[a]					
34:55	0.0488	0.0473	0.0461	0.0444	0.0404	0
34:56	0.0204	0.0201	0.0197	0.0192	0.0177	0
34:66	0[a]					
34:77	0[a]					
44:44	0.8905[a]					
44:55	0.2470	0.2632	0.2713	0.2774	0.2869	0.3156
44:56	0.2118	0.2289	0.2366	0.2440	0.2573	0.2945
44:66	0.7945[a]					
44:77	0.7945[a]					
55:55	0.1593	0.1839	0.1954	0.2063	0.2238	0.2695
55:56	0.0805	0.0996	0.1092	0.1177	0.1334	0.1853
55:66	0.2490	0.2729	0.2828	0.2916	0.3072	0.3523
55:77	0.2357	0.2551	0.2633	0.2706	0.2830	0.3156

a. Values are the same for all bond angles.

Table 14. (Continued)

Integral	H-O-H bond angle (degrees)					
	90	100	105	110	120	180
56:56	0.0858	0.1009	0.1083	0.1147	0.1289	0.1711
56:66	0.2326	0.2526	0.2619	0.2708	0.2870	0.3339
56:77	0.2083	0.2256	0.2337	0.2413	0.2551	0.2945
66:66	0.8905[a]					
66:77	0.7945[a]					
77:77	0.8905[a]					
57:57	0.0092	0.0103	0.0107	0.0113	0.0123	0.0185
57:67	0.0104	0.0123	0.0116	0.0120	0.0127	0.0147
67:67	0.0480[a]					
15:15	0.1315	0.1422	0.1468	0.1511	0.1584	0.1768
15:16	0.0911	0.0948	0.0963	0.0982	0.1019	0.1053
15:25	0.0002	0.0003	0.0003	0.0003	0.0004	0.0005
15:26	0.0079	0.0086	0.0089	0.0092	0.0097	0.0112
15:35	0.0399	0.0465	0.0487	0.0507	0.0538	0.0622
15:36	0.0763	0.0826	0.0856	0.0883	0.0934	0.1078
15:45	0.0168	0.0149	0.0129	0.0121	0.0099	0
15:46	0.0223	0.0219	0.0215	0.0209	0.0193	0
16:16	0.0758	0.0789	0.0803	0.0827	0.0849	0.0951
16:25	0.0057	0.0062	0.0064	0.0067	0.0072	0.0101
16:26	0.0193	0.0197	0.0199	0.0201	0.0205	0.0217

a. Values are the same for all bond angles.

Table 14. (Continued)

Integral	H-O-H bond angle (degrees)					
	90	100	105	110	120	180
16:35	0.0268	0.0299	0.0312	0.0326	0.0350	0.0412
16:36	0.1125	0.1160	0.1177	0.1194	0.1227	0.1329
16:45	0.0208	0.0200	0.0198	0.0194	0.0181	0
16:46	0.0139	0.0132	0.0128	0.0123	0.0111	0
25:25	0.0001	0.0001	0.0001	0.0001	0.0001	0.0002
25:26	0.0013	0.0014	0.0015	0.0015	0.0016	0.0018
25:35	0.0009	0.0010	0.0011	0.0012	0.0013	0.0018
25:36	0.0022	0.0024	0.0025	0.0026	0.0027	0.0032
25:45	0.0010	0.0015	0.0017	0.0020	0.0023	0
25:46	0.0006	0.0006	0.0006	0.0006	0.0005	0
26:26	0.0264[a]					
26:35	0.0062	0.0067	0.0069	0.0071	0.0075	0.0087
26:36	0.0349[a]					
26:45	0.0025	0.0025	0.0024	0.0023	0.0022	0
26:46	0[a]					
35:35	0.0216	0.0216	0.0236	0.0267	0.0288	0.0433
35:36	0.0466	0.0505	0.0523	0.0540	0.0571	0.0659
35:45	0.0106	0.0107	0.0104	0.0102	0.0093	0
35:46	0.0089	0.0087	0.0086	0.0083	0.0077	0
36:36	0.1749[a]					

a. Values are the same for all bond angles.

Table 14. (Continued)

Integral	H-O-H bond angle (degrees)					
	90	100	105	110	120	180
36:45	0.0204	0.0201	0.0197	0.0192	0.0177	0
36:46	0[a]					
45:45	0.0068	0.0067	0.0052	0.0049	0.0036	0.0185
45:46	0.0139	0.0144	0.0146	0.0147	0.0149	0.0147
46:46	0.0480[a]					
17:17	0.0478	0.0467	0.0463	0.0457	0.0447	0.0385
17:27	0.0168[a]					
17:37	0.0921[a]					
17:47	0.0104	0.0094	0.0089	0.0084	0.0073	0
27:27	0.0265[a]					
27:37	0.0349[a]					
27:47	0[a]					
37:37	0.1750[a]					
37:47	0[a]					
47:47	0.0480[a]					

a. Values are the same for all bond angles.

Table 15. Bare nuclear field integrals over symmetry orbitals (a.u.)

Integral	H-O-H bond angle (degrees)					
	90	100	105	110	120	180
(O:11)	0.7648	0.7418	0.7315	0.7221	0.7057	0.6672
(O:12)	0.3328[a]					
(O:13)	0.5550[a]					
(O:14)	0.2501	0.2273	0.2153	0.2028	0.1768	0
(O:22)	7.7000[a]					
(O:23)	-1.0505[a]					
(O:24)	0[a]					
(O:33)	1.2636[a]					
(O:34)	0[a]					
(O:44)	1.1375[a]					
(O:55)	0.2568	0.2798	0.2901	0.2995	0.3159	0.3544
(O:56)	0.2501	0.2709	0.2806	0.2897	0.3063	0.3537
(O:66)	1.1375[a]					
(O:77)	1.1375[a]					
(H:11)	0.9663	0.9133	0.8910	0.8711	0.8381	0.7613
(H:12)	0.0486	0.0484	0.0483	0.0482	0.0481	0.0477
(H:13)	0.4465	0.4402	0.4366	0.4331	0.4281	0.4112
(H:14)	0.3381	0.3060	0.2889	0.2727	0.2387	0
(H:22)	0.5524[a]					

a. Values are the same for all bond angles.

Table 15. (Continued)

Integral	H-O-H bond angle (degrees)					
	90	100	105	110	120	180
(H:23)	-0.0005[a]					
(H:24)	0.0117	0.0106	0.0100	0.0095	0.0083	0
(H:33)	0.5451[a]					
(H:34)	0.1290	0.1172	0.1110	0.1046	0.0912	0
(H:44)	0.5661	0.5553	0.5501	0.5449	0.5352	0.5043
(H:55)	0.4160	0.4420	0.4529	0.4625	0.4784	0.5140
(H:56)	0.2434	0.2667	0.2782	0.2882	0.3071	0.3662
(H:66)	0.5661	0.5768	0.5821	0.5872	0.5970	0.6279
(H:77)	0.5043[a]					

a. Values are the same for all bond angles.

C. Results and Interpretations

1. General considerations

Utilizing the notation for MO's defined in equations (3.10), the ground state MO electronic configuration for H_2O may be written in general as follows:

$$H_2O: \quad 1a_1)^2 2a_1)^2 1b_2)^2 3a_1)^2 1b_1)^2 \ , \ {}^1A_1 \ . \qquad (3.55)$$

The MO's are given in their order of increasing energy, as determined by qualitative considerations indicated in Chapter II.

The SCF calculations were carried out, therefore, under the assumption that three MO's of A_1 symmetry and one MO each of B_1 and B_2 symmetries are occupied in the ground state. There seem to be no arguments to the effect that this general assignment is not true. If, however, this configuration were not correct for the ground state, the final results would be meaningless to a large degree. One must have a good approximation of the ground state of a molecule before it is possible to determine an excited state of the same symmetry. It is expected, although by no means proven, that if one made the wrong choice of occupied MO's, the calculated results would indicate unoccupied

orbitals lower in energy than the originally assumed occupied ones.

The ground state LCAO MO's, listed along with the unoccupied orbitals in the matrix (3.10), may be rewritten in the following more useful notation:

$$\begin{aligned}
\phi(1a_1) &= c_{11}\sigma_1 + c_{12}{}^{o} + c_{13}{}^{s} + c_{14}{}^{z} \\
\phi(2a_1) &= c_{21}\sigma_1 + c_{22}{}^{o} + c_{23}{}^{s} + c_{24}{}^{z} \\
\phi(3a_1) &= c_{31}\sigma_1 + c_{32}{}^{o} + c_{33}{}^{s} + c_{34}{}^{z} \qquad (3.56) \\
\phi(1b_2) &= c_{55}\sigma_5 + c_{56}{}^{y} \\
\phi(1b_1) &= x \ ,
\end{aligned}$$

where σ_1 and σ_5 are defined as in equation (3.9).

It is important now to distinguish more carefully the two treatments that were carried out. First of all, a complete SCF treatment was performed which included no assumptions beyond those contained in the LCAO MO's defined as in (3.10) (except, of course, the three-center integral approximations). As was noted in Part A of this chapter, the seven-by-seven secular equation (3.21) reduced to one four-by-four, one two-by-two and one one-by-one equations on account of symmetry. In addition, a second calculation was carried out in which the following LCAO coefficients were

assumed to be identically equal to zero: c_{11}, c_{13}, c_{14}, c_{22} and c_{32}. The secular equation was thereby simplified to one three-by-three, one two-by-two and two one-by-one determinants. Hereafter, this latter calculation will be referred to as the approximate treatment.

The MO $\phi(1a_1)$ is not orthogonal to $\phi(2a_1)$ and $\phi(3a_1)$ in this approximate treatment. Since the methods of calculation have been derived under the condition that all MO's are strictly orthogonal, the numerical results of this treatment should be viewed with some discretion. Inasmuch as the degree of non-orthogonality is expected to be small due to the small overlap between the oxygen and hydrogen 1s AO's, the results should not be entirely meaningless. A direct comparison of the two treatments should be of interest in view of the fact that this assumption of no inner-shell-outer-shell mixing is, indeed, utilized quite extensively.

The requirement of a minimum amount of 1s-2s-2p mixing in order to maintain MO-orthogonality has been called forced hybridization by Mulliken (108). In the approximate treatment, the neglect of this type of hybridization could have been compensated for either by permitting the coefficient c_{11} or the coefficients c_{22} and c_{32} to take on non-zero values. In either case, the simplification of the secular equation secured in the approximate treatment

would be lost. Therefore, in the complete treatment, the full measure of inner-shell-outer-shell mixing was introduced; that is, all of the ground state LCAO coefficients in (3.56) were allowed to assume non-zero values. This mixing which is introduced over and beyond the minimum requirements expressed by forced hybridization might not be expected to lead to an extensive improvement of the wave function. Some gain must be secured, but it is more likely that higher energy AO's, such as 2p hydrogen and 3s oxygen functions, would be more valuable in this respect.

2. The ground-state MO's

In Table 16 are listed the SCF LCAO coefficients for the ground state MO's (see equations 3.56) as a function of the H-O-H bond angle. Also given are the coefficients for the MO's which are unoccupied in the ground state electronic configuration. The results are tabulated for both the approximate (A) and complete (C) treatments.

A general perusal of the values, say of the 105 degree treatment, gives an indication of the nature of the MO's. The orbital $\phi(2a_1)$, which was assumed in simple MO considerations to be a pure 2s oxygen AO, here appears to be rather bonding. A measure of negative charge has been concentrated between the positive nuclei, thus leading to a lowering of the energy (109). The $\phi(3a_1)$ MO,

Table 16. LCAO SCF MO's for the ground state of H_2O

Coefficients	H-O-H bond angle (degrees)					
	90		100		105	
	A[a]	C[b]	A	C	A	C
Occupied orbitals						
c_{11}'	0	-0.0031	0	-0.0032	0	-0.0033
c_{11}	0	-0.0037	0	-0.0038	0	-0.0039
c_{12}	1	1.0002	1	1.0002	1	1.0002
c_{13}	0	0.0161	0	0.0162	0	0.0163
c_{14}	0	0.0026	0	0.0025	0	0.0024
c_{21}'	0.202	0.175	0.2073	0.179	0.207	0.1781
c_{21}	0.243	0.210	0.245	0.211	0.243	0.2088
c_{22}	0	-0.028	0	-0.029	0	-0.0286
c_{23}	0.821	0.842	0.8188	0.842	0.821	0.8450
c_{24}	0.133	0.149	0.1257	0.139	0.120	0.1328
c_{31}'	0.502	0.397	0.452	0.348	0.438	0.3341
c_{31}	0.603	0.477	0.534	0.411	0.514	0.3917
c_{32}	0	-0.031	0	-0.027	0	-0.0258
c_{33}	-0.618	-0.533	-0.569	-0.481	-0.548	-0.4601
c_{34}	0.674	0.759	0.736	0.810	0.757	0.8277
c_{55}'	0.737	0.781	0.738	0.780	0.736	0.7759
c_{55}	0.550	0.582	0.574	0.606	0.582	0.6136
c_{56}	0.618	0.585	0.587	0.554	0.575	0.5428
Unoccupied orbitals						
c_{41}'		1.011		1.048		1.061
c_{41}		1.215		1.238		1.244
c_{42}		-0.082		-0.085		-0.086
c_{43}		-0.774		-0.819		-0.833
c_{44}		-0.741		-0.671		-0.642
c_{65}'		1.300		1.247		1.230
c_{65}		0.969		0.969		0.973
c_{66}		-0.967		-1.000		-1.013

a. Approximate treatment.

b. Complete treatment.

Table 16. (Continued)

Coefficients	H-O-H bond angle (degrees)					
	110		120		180	
	A[a]	C[b]	A	C	A	C
Occupied orbitals						
c_{11}'	0	-0.0033	0	-0.0035	0	-0.0038
c_{11}	0	-0.0038	0	-0.0040	0	-0.0042
c_{12}	1	1.0002	1	1.0002	1	1.0002
c_{13}	0	0.0163	0	0.0165	0	0.0169
c_{14}	0	0.0023	0	0.0021	0	0
c_{21}'	0.204	0.175	0.204	0.1740	0.224	0.1785
c_{21}	0.237	0.204	0.235	0.2001	0.250	0.1988
c_{22}	0	-0.028	0	-0.0283	0	-0.0289
c_{23}	0.825	0.849	0.829	0.8542	0.824	0.8632
c_{24}	0.115	0.127	0.103	0.1129	0	0
c_{31}'	0.426	0.322	0.386	0.2835	0	0
c_{31}	0.496	0.375	0.444	0.3260	0	0
c_{32}	0	-0.025	0	-0.0220	0	0
c_{33}	-0.528	-0.440	-0.477	-0.3884	0	0
c_{34}	0.777	0.843	0.823	0.8802	1	1
c_{55}'	0.740	0.777	0.748	0.7821	0.781	0.7863
c_{55}	0.594	0.624	0.616	0.6438	0.681	0.6852
c_{56}	0.560	0.529	0.531	0.5014	0.444	0.4378
Unoccupied orbitals						
c_{41}'		1.072		1.093		1.145
c_{41}		1.248		1.257		1.257
c_{42}		-0.087		-0.089		-0.093
c_{43}		-0.844		-0.870		-0.955
c_{44}		-0.612		-0.541		0
c_{65}'		1.213		1.185		1.147
c_{65}		0.974		0.975		1.0000
c_{66}		-1.028		-1.055		-1.130

a. Approximate treatment.

b. Complete treatment.

although still having bonding characteristics, now contains a negative oxygen hybrid (110). The coefficient of 2s must be negative in order to make this MO orthogonal to $\phi(2a_1)$. This adds electronic density to the negative lobe of 2pz and subtracts from the positive lobe. Consequently, there is a smaller concentration of charge between the nuclei than if no 2s were present in $\phi(3a_1)$. This is relevant to Mulliken's conclusion (108) that forced hybridization leads to weakening of/bonding MO's. Here, the comparison is being made between the most simple MO formulation in which no 2s-2p mixing is allowed in $\phi(3a_1)$ and the present approximate treatment. A calculation carried out on the former model would undoubtedly indicate that $\phi(3a_1)$ is a strongly bonding orbital. Forced hybridization with respect to the assumed inner 2s shell would lessen this bonding power. Further 2s-2p mixing equivalent to the approximate treatment probably lessens the bonding in $\phi(3a_1)$ but strengthens the bonding in $\phi(2a_1)$ (see page 33).

As was indicated qualitatively in Chapter II, $\phi(1b_2)$ is probably the most strongly bonding valence shell MO for the H-O-H bond angle of 105 degrees. This is postulated because of the weakened $\phi(3a_1)$ bonding due to forced hybridization and because of the more pronounced overlap which can be attained in $\phi(1b_2)$ at large bond angles.

In regard to the variation of the MO's with respect to

bond angle, the following qualitative statements may be made (39): at a bond angle of zero degrees, $\phi(1b_1)$ becomes a pure 2pπ (y) AO on oxygen (with the real possibility of bonding with a 2pπ helium AO, which is the united atom function corresponding to σ_5), and $\phi(3a_1)$ probably is quite bonding; at 180 degrees, $\phi(1b_2)$ takes on the greatest responsibility for bonding, while $\phi(3a_1)$ becomes a pure 2pπ (z) AO on oxygen.

It is interesting to note that for the bond angle of 105 degrees the ratio of the LCAO coefficients in $\phi(1b_2)$ is opposite to that which is to be expected on the basis of the relative electroaffinity of oxygen and hydrogen (see page 27). One might expect that such a basis for predicting LCAO MO coefficients would only be justified if there were one valence orbital. In the case of H_2O, the orbitals tend to correlate themselves in a manner which is governed only by the relative electroaffinity in a gross sense. The 2s-2pz hybridization allows considerable charge transfer in $\phi(3a_1)$, while the electrons in $\phi(1b_2)$ tend to avoid the latter as well as going into the O-H bonding regions.

It is seen that the differences between the approximate and complete treatments are, indeed, considerable and quite significant in some cases. The difference between the coefficients of σ_1 in $\phi(3a_1)$, the most extreme case,

is 26 per cent, while the average variation of all coefficients in the 105 degree calculation is about 11 per cent.

3. Total energy and sources of error

The total ground state SCF electronic energies are given in Table 17 as a function of bond angle for both the approximate and complete treatments. Also listed are the nuclear repulsion, total molecular and dissociation energies. The latter are obtained by subtracting the theoretically calculated total energy of the separated atoms from the total SCF molecular energies. The electronic energy of the oxygen atom, -2054.8 electron volts, was computed using the same orthogonalized Slater AO's as were used for the MO calculations.

Also listed in Table 17 are the corresponding experimental energies for H_2O.

It is seen that these calculations indicate that the minimum molecular energy occurs at a bond angle somewhat greater than 120 degrees. This quite divergent result should probably not be considered as serious as it might first appear. The total electronic energy is the quantity which is actually minimized by the SCF procedure. It is found to differ from the observed value by only about 0.75 per cent, although the absolute difference is quite considerable. As the bond angle decreases from 180 to

Table 17. Total SCF energies for the ground state of H_2O

H-O-H bond angle (deg.)	Type of treatment	Total electronic energy (e.v.)	Nuclear repulsion energy (e.v.)	Total molecular energy (e.v.)	Dissoc. energy (e.v.)
90	A[a]	-2315.0	251.06	-2063.9	9.1
	C[a]	-2313.0	251.06	-2061.9	7.1
100	A	-2314.4	250.25	-2064.1	9.3
	C	-2312.6	250.25	-2062.3	7.5
105	A	-2314.2	249.91	-2064.2	9.4
	C	-2312.4_4	249.91	-2062.5_3	7.7
105	Exp.	-2329.8	249.91	-2079.9[b]	9.49[b]
110	A	-2314.0	249.61	-2064.4	9.6
	C	-2312.4	249.61	-2062.8	8.0
120	A	-2313.7	249.11	-2064.6	9.8
	C	-2312.1_4	249.11	-2063.0_3	8.2
180	A	-2310.6	247.95	-2062.6	7.8
	C	-2309.9	247.95	-2062.0	7.2

a. A = approximate treatment, C = complete treatment.

b. Experimental dissociation energy from (22, p. 481); observed total atomic energies from (111).

90 degrees, the electronic energy decreases by only about 0.13 per cent. The variable part of this large quantity is thus very small.

Moffitt (5,112) has recently discussed to some length the inadequacies of the present orbital theories with regard to energy calculations. His arguments are quite relevant to the results of this calculation. It seems quite evident that if one is interested in determining the equilibrium bond angle, the proper procedure would be to maximize the dissociation energy, a quantity which exhibits a relatively pronounced variation with bond angle. It appears rather strange to attempt an accurate calculation of the difference between two large quantities which are in themselves almost twice as inaccurate as that difference.

There are several other possible causes for the divergence of the calculated equilibrium bond angle from the observed value. Most of these points are applicable in general to the whole problem as being sources of error. They are considered here because of their special relation to the total energy problem.

The possibility that CI (see page 9) may be of importance should be considered. This question is discussed in detail in a following section. It is found tentatively that CI to a certain approximation is of negligible importance and is not able to account for the above discrepancy

between theory and experiment.

Another possibility is that the LCAO approximation is poor with respect to this total energy calculation. One might expect the best AO's to be quite different for small bond angles than for large. It has always been hoped in MO calculations that variation of the LCAO coefficients alone would sufficiently account for any required changes in the orbitals. The question of better Z-values for the AO's as well as the addition of higher energy orbitals is especially relevant in this respect.

It must also be remembered that these calculations were carried out only for the experimental value of the O-H bond distance. There is some possibility that the computed total molecular energy minimum lies at some other bond angle, say less than 120 degrees, and some O-H bond distance differing from 0.9580 angstroms.

The approximate values used for many of the three-center integrals may, of course, be held accountable for the large calculated equilibrium bond angle. The errors involved in these approximations are of a magnitude to be of real importance. For H_2O, there are several large three-center integrals involving either the 2pz or 2py AO's which vary quite considerably with bond angle. A partial test of the effect of these approximations on the total energy was carried out. This is treated in detail

in section 9. It was found that the possible errors contained in the three-center integrals may very well be responsible for the divergent results in the dissociation energy calculation.

Finally, it should be noted that there was the ever-present possibility of numerical error in as long and tedious a calculation as was attempted here. Every precaution was taken to reduce these possibilities to a minimum. Once the integrals were evaluated and checked several times, and the basic calculations set up, the nature of the SCF procedure makes any further error a practical impossibility.

4. The dipole moment

Using the SCF MO's from the complete treatment given in Table 16, the dipole moment of H_2O was calculated for all bond angles. The results are given in Table 18, and the details of the computation are furnished in Appendix D.

The computed dipole moment is one of the important criteria for judging the accuracy of a wave function. It is seen that the result for the observed H-O-H bond angle is in quite good agreement with the experimental value of 1.84 D.

The dipole moment was also computed using the MO's

from the approximate treatment. The result is 1.21 D. This value was obtained, however, by assuming that all of the MO's are orthogonal. If this approximation is valid, it could be stated that the improvement of the wave

Table 18. The calculated dipole moment of the ground state of H_2O

H-O-H bond angle (degrees)	Dipole moment (Debye units)
90	1.53[a]
100	1.55
105	1.52
110	1.45
120	1.32
180	0

a. All values directed in the sense $H_2^+O^-$.

function on going from the approximate to the complete treatment is quite astonishing.

5. Ionization energies

An SCF orbital energy should represent a good approximation to the negative of the corresponding experimental I (1,6). In Table 19, the orbital energies are listed for both the approximate and complete treatments for all bond angles. Also given are the observed I's as well as the SCF

Table 19. LCAO SCF orbital energies for the ground state of H_2O (e.v.)

MO	H-O-H bond angle (degrees)						Observed
	90		100		105		
	A[a]	C[b]	A	C	A	C	
$\epsilon(1a_1)$	-560.08	-558.09	-559.37	-557.52	-559.12	-557.27	
$\epsilon(2a_1)$	-38.19	-36.86	-37.65	-36.40	-37.43	-36.19	
$\epsilon(1b_2)$	-18.7	-17.8	-18.9	-18.3	-19.2	-18.55	-16.2±0.3[c,d]
$\epsilon(3a_1)$	-15.5	-14.2	-14.6	-13.6	-14.2	-13.20	-14.5±0.3[c,e]
$\epsilon(1b_1)$	-13.4	-12.2	-13.0	-11.9	-12.8	-11.79	-12.6±0.1[c,f]
$\epsilon(4a_1)$		12.1		13.6		13.7	
$\epsilon(2b_2)$		16.1		15.9		15.9	

a. Approximate treatment.

b. Complete treatment.

c. Negatives of ionization potentials obtained by electron impact (48).

d. Spectroscopic value: 16.0 ± 0.5 e.v. (49).

e. No spectroscopic value recorded.

f. Spectroscopic value: 12.56 ± 0.01 e.v. (50).

Table 19. (Continued)

MO	H-O-H bond angle (degrees)					
	110		120		180	
	A[a]	C[b]	A	C	A	C
$\epsilon(1a_1)$	-558.96	-557.17	-558.58	-556.83	-556.08	-554.80
$\epsilon(2a_1)$	-37.30	-36.07	-36.92	-35.75	-34.79	-34.11
$\epsilon(1b_2)$	-19.5	-18.9	-19.9	-19.48	-21.0	-20.78
$\epsilon(3a_1)$	-14.0	-13.0	-13.4	-12.60	-11.3	-10.80
$\epsilon(1b_1)$	-12.8	-11.8	-12.5	-11.64	-11.3	-10.80
$\epsilon(4a_1)$		14.0		14.5		14.4
$\epsilon(2b_2)$		15.7		15.3		15.8

a. Approximate treatment.

b. Complete treatment.

orbital energies for the unoccupied MO's.

There is little doubt that the first observed value corresponds to removal of a non-bonding 2px electron. The calculated value is too low because the correlation energy for the resulting H_2O^+ ion, calculated using ground state orbitals, is less than that for the ground state itself. In other words, there is an excessive amount of electronic repulsion encountered in $(2px)^2$ in the orbital picture of H_2O due to the inability of the electrons to avoid each other. This is not encountered in the resulting H_2O^+ ion. Quantitative justification is given for this fact by the correlation energies for the resulting dissociation products. The calculated energy of O^+ ($1s^2 2s^2 2p^3$, ^4S) is 11.5 electron volts above the observed and of O ($1s^2 2s^2 2p^4$, ^3P) is 15.7 electron volts above the true energy. The appropriate valence state correlation energies are comparable to these.

It is somewhat disturbing that upon molecule formation, the valence state I of the oxygen atom, O ($1s^2 2s^2 2p^4$, V_2) $\rightarrow$ O^+ ($1s^2 2s^2 2p^3$, V_3), calculated to be about 10 electron volts, is raised to the corresponding molecular ionization potential of 11.8 electron volts. This is directly opposed in direction to that which is observed: 14.7 to 12.6 electron volts. The latter has generally been attributed to charge transfer effects, a

phenomenon which also certainly takes place in the theoretical results, but apparently does not manifest itself in this manner. The difficulty can be explained in terms of correlation energies, a factor which certainly reminds one of the strong objections voiced by Moffitt concerning the energy calculations of present orbital theories (5,112). The calculated energy of H_2O^+, using H_2O SCF ground state MO's, is very poor relative to that of O^+, using oxygen atom Slater AO's, whereas the correlation energies for H_2O and O are comparable in magnitude.

It has been noted by Mulliken (59) that $\phi(1b_1)$ may be weakly bonding, as attested by the large π-π overlap; $S(2p\pi_{h'}, 2p\pi_o)$ equals 0.19. This is also indicated experimentally in OH by the increase of internuclear distance by 0.058 angstroms upon removal of the π-electron.

There exists some question concerning the assignment of the higher ionization potentials (48). These calculations favor the designations as listed in Table 19. The numerical agreement is not as satisfactory as one might like, although the order of assignment seems quite well determined. It is possible that the use of exact values of three-center integrals would bring about better agreement with the observed I's, but it is doubtful that the order would be reversed. The discussion on pages 33-36 is especially pertinent in this regard. A significant difference

between the potentials for $\phi(1b_2)$ and $\phi(3a_1)$ exists even at 90 degrees. It is interesting to note that there is a two electron-volt difference between the second and third I's of H_2S (48), in which the equilibrium bond angle is about 92 degrees.

As was also noted in Mulligan's treatment of CO_2 (66), considerably higher I's are calculated for the non-valence shells than those predicted by Mulliken. The value for $\phi(2a_1)$ is partially explained by the fact that Mulliken took this orbital to be non-bonding (I ~ 32 electron volts), whereas the SCF function turns out to be quite bonding.

The variance of the computed orbital energy of $\phi(1a_1)$ from the observed K-shell X-ray absorption limit for the oxygen atom (524 electron volts) is due to the choice of the Slater 1s orbital; the calculated valence state ionization potential $O(1s^2 2s^2 2p^4, V_2) \rightarrow O^+(1s 2s^2 2p^4, V_3)$ using Slater orbitals, is 557.1 electron volts.

6. The effect of configuration interaction

In MO calculations, the question of the importance of CI often arises. For low excited states, interaction of this type is expected to be quite considerable since there are liable to be many states of the same symmetry in the same energy range. For the ground state of a molecule,

however, CI should be of little importance. However, some calculations were carried out to test this assumption.

The first question to be considered concerns the choice of excited state wave functions to be utilized in the CI calculation. Roothaan (1) has discussed this in some detail in connection with the calculation of excitation energies. It is assumed that the SCF ground state MO's may be used. For H_2O, $\phi(4a_1)$ and $\phi(2b_2)$ are suitable excited state MO's, their LCAO forms being determined completely by orthonormality conditions.

If the assumption in the preceding paragraph is accepted, it can be shown that totally symmetric states which differ from the H_2O ground state by only a one electron transition exhibit zero interaction with the ground state. If any other MO's were used, CI would be of importance.

Two of the lowest excited states which do interact with the ground state function in this approximation were considered individually. They were

$$\begin{aligned} \Phi_1 &: (1a_1)^2(2a_1)^2(3a_1)^2(1b_2)^2(4a_1)^2 , \\ \Phi_2 &: (1a_1)^2(2a_1)^2(3a_1)^2(1b_2)^2(2b_2)^2 . \end{aligned} \tag{3.57}$$

The results of the CI are given in Table 20. It is seen that Φ_1 gives zero interaction with the ground state Φ_o,

and Φ_2 shows a slight, but still negligible interaction. The coefficients were not numerically determined, since it is quite obvious that a and c must be almost unity and b and d must be nearly zero.

Table 20. Effect of configuration interaction

Wavefunction[a]	Total electronic energy (a.u.)
Φ_o	-84.004
$a\Phi_o + b\Phi_1$	-84.004
$c\Phi_o + d\Phi_2$	-84.005

a. See equation (3.57).

7. The equivalent orbitals

As was discussed in Chapter II, J. A. Pople (53) utilized the EO (equivalent orbital) method of Lennard-Jones (54 - 57) in a semi-empirical manner to study the electronic structure of H_2O. Some modifications of the numerical treatment have recently been published by A. B. F. Duncan and J. A. Pople (58).

The SCF MO's from the complete treatment were transformed rigorously to the EO representation. The results,

together with the values given by Duncan and Pople, are given in Table 21. The orbitals $\phi(b_{\pm})$ denote bond EO's, the plus sign for the orbital directed to h', the negative sign for that directed to h". The lone-pair EO's $\phi(l_{\pm})$ are directed to the backside of the oxygen atom. They are symmetric with respect to the xz-plane, one orbital directed above the plane of the molecule, the other below the plane.

It is immediately interesting to compare the values given for the lone-pair EO's at 105 degrees with the analogous hybridized AO's calculated by the magic formula. Such a comparison might be subject to some criticism, since the latter method is essentially based on VB theory. The analogy between the lone-pair functions, however, seems to be quite reasonable. It is seen that the results of the magic formula for these electrons lie intermediate between those of the present calculation and those by Duncan and Pople.

On the basis of the SCF results, complete localization of bond EO's seems to be unjustified. Also, the assumption that these orbitals are aligned with the bond axis appears to be a restriction which is not entirely substantiated by the SCF calculations nor the magic formula results. In fact, the angle between the SCF bond functions, as indicated by the coefficients of 2pz and 2py, appears to

Table 21. The EO's for the ground state of H_2O

EO	AO	90	105			120	180
		SCF	SCF	Duncan-Pople[a]	Magic Formula[b]	SCF	SCF
$\phi(b_1)$	h'	0.607	0.577	0.58	0	0.557	0.482
	h"	-0.174	-0.199	0	0	-0.225	-0.304
	o	-0.028	-0.026	0	0	-0.024	-0.020
	s	-0.105	-0.006	0.06	0.29	0.082	0.610
	z	0.534	0.561	0.37	0.65	0.572	0
	y	±0.414	±0.384	±0.49	±0.71	±0.355	±0.310
$\phi(l_1)$	o	-0.009	-0.009	0	0	-0.009	0
	s	0.697	0.680	0.58	0.65	0.658	0
	z	-0.120	-0.192	-0.41	-0.29	-0.258	-0.707
	x	±0.707	±0.707	±0.71	±0.71	±0.707	±0.707

a. Adapted from results of Duncan and Pople (58).

b. Derived from values given in equation (2.43).

decrease as the bond angle increases. Bond localization is exact for a bond angle of zero degrees, and poorest for 180 degrees. For this reason, inspection of the variation of EO bond properties as a function of angle is probably questionable.

The dipole moment arising from the lone-pairs is found to be 1.69 D as compared to the Duncan and Pople value of 3.03 D. The total bond dipole is -5.77 D while the other workers' result was -6.82 D. The moment due to the hydrogen nuclei is 5.60 D.

8. The first singlet electronic excited state

Utilizing the same excited SCF function for $\phi(4a_1)$ as was utilized in the CI calculation, it is possible to calculate the excitation energy, as well as the corresponding oscillator strength, for the lowest predicted electronic transition. This involves the promotion of one electron from the $\phi(1b_1)$ MO to the unoccupied $\phi(4a_1)$ orbital:

$$(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2 \ , \ {}^1A_1$$
$$(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)(4a_1) \ , \ {}^{1,3}B_1 \ . \qquad (3.58)$$

There are three absorption peaks in the vacuum ultraviolet at 1608, 1648 and 1718 angstroms (113) which might be

attributed to this transition. It is interesting to note that the two energy separations between successive bands are both about 1500 wave numbers, which nearly equals the fundamental frequency for the symmetrical bending vibration (29, p. 281).

The calculated energy for the transition (3.58), using SCF ground state MO's, is 96,200 wave numbers. The absorption would then occur at 1040 angstroms. The result is not expected to be very accurate, since the approximation of $\phi(4a_1)$ is certainly of doubtful validity.

Mulliken (40) takes the excited MO $\phi(4a_1)$ to be a pure oxygen 3s AO. Since this higher energy AO was not used in the present LCAO set, it is quite likely that the computed orbital which has been used here is quite invalid.

Oscillator strengths for the transition (3.58) were also computed. The dipole length method may be formulated as follows:

$$f = \nu(1.085 \times 10^{11}) \left[\int (1b_1)\underline{x}(4a_1)\,dv \right]^2 , \qquad (3.59)$$

where the frequency of the transition, ν, is in wave numbers and the integral is in centimeters. The resulting value is 3×10^{-6}. The dipole velocity method,

$$f = (1.464 \times 10^{5}) \left[\int (1b_1)(d/dx)(4a_1)\,dv \right]^2 / \nu , \qquad (3.60)$$

where ν is in wave numbers and the integral is in inverse atomic units, gives the result 0.037. In both calculations, the theoretically calculated value for ν was utilized. If the experimental frequency of transition ν were used in (3.59) and (3.60), the results would be changed to 1.89×10^{-6} and 0.059, respectively. The experimentally observed f number is 0.03 (113).

The dipole length method seemingly gives a very poor result. This may very well be attributed to the fact that no 3s character has been included in the excited state function. The 3s AO, with its r^2-dependence and exponential part undoubtedly containing a low Z-value, would probably predominate at large distances. But it is at large distances where the dipole length method is most sensitive. The absence of 3s character from $\phi(4a_1)$ would cause the resulting computed f number to be low.

These predictions were partially substantiated by some simple calculations based upon the assumption that the transition (3.58) is simply (2px) → (3s). Slater AO's were utilized, the Slater Z-value for 3s being 1.75. Using the experimental value for ν, the dipole length method gave the more reasonable result of 0.016, while the dipole velocity value was 0.191.

Integrals required for the dipole length method as given in equation (3.59) may be found in Appendix D. The

additional integral involving the 3s AO may be formulated as follows:

$$\int(2px)\underline{x}(3s)dv = 64(10)^{1/2}\mu_2^{5/2}\mu_3^{7/2}(\mu_2+\mu_3)^{-7} = 0.2929 \text{ a.u.} \tag{3.61}$$

The integrals for the dipole velocity calculation are given by H. Shull (114), with the exception of the integral involving 3s, which is given as follows:

$$\int(3s)(d/dx)(2px)dv = 32(10)^{1/2}\mu_2^{5/2}\mu_3^{7/2}(5)^{-1}(\mu_3+\mu_2)^{-5}. = 0.2815 \text{ a.u.} \tag{3.62}$$

9. Dependence of the results on approximate integrals

In addition to the SCF calculations originally carried out and described in the preceding pages, a second complete treatment for the bond angle of 105 degrees was performed. In this computation, the values for two of the approximate three-center integrals were revised as follows:

$$\begin{aligned}(H'':h'z): &\quad 0.1581 \rightarrow 0.1337 \\ (h''h'':h'z): &\quad 0.1400 \rightarrow 0.1028\ ,\end{aligned} \tag{3.63}$$

where values are given in atomic units.

Table 22. Results of complete SCF treatment using revised values of integrals

	First complete calculation	Revised complete calculation
LCAO coefficients		
c_{21}'	0.178	0.176
c_{22}	-0.029	-0.028
c_{23}	0.845	0.848
c_{24}	0.133	0.130
c_{31}'	0.334	0.339
c_{32}	-0.026	-0.026
c_{33}	-0.460	-0.460
c_{34}	0.828	0.826
c_{55}	0.776	0.814
c_{56}	0.543	0.511
Orbital energies[a]		
$\epsilon(1a_1)$	-557.3	-558.6
$\epsilon(2a_1)$	-36.2	-36.8
$\epsilon(3a_1)$	-13.2	-14.0
$\epsilon(1b_2)$	-18.6	-19.4
$\epsilon(1b_1)$	-11.8	-12.5
Total energies[a]		
Electronic	-2312.4	-2312.8
Molecular	-2062.5	-2062.9
Dissociation	7.7	8.1

a. Values given in electron volts.

These two were chosen since their probable error was considered to be relatively high. Also, it is quite possible that the minimum molecular energy is quite dependent upon these integrals as well as upon the analogous integrals containing 2py instead of 2pz. It should be noted that the above revisions were probably somewhat overemphasized.

The complete results, with the exception of the LCAO coefficients for $\phi(1a_1)$ which were unchanged, are given in Table 22. It is significant that the A_1 MO's have changed very little, but the B_2 orbital has changed quite considerably. The orbital energies also have undergone rather noticeable variations. The total molecular energy has been depressed to a value which is almost equal to the energy of the 120 degree configuration in the original calculation. It would be interesting to determine whether or not the energy minimum is actually shifted to smaller angles by the introduction of these revised integrals.

The revised calculation thus emphasizes the need for exact values of three-center integrals if a real test of this theory is to be carried out. Up to the present, the usual emphasis has been merely to include all integrals whether they are approximated or not.

IV. CONCLUSIONS

The major conclusions derived from the foregoing research may be listed as follows:

1. The most simple MO and VB approximations present an inadequate understanding of the properties of H_2O.
2. The Principle of Maximum Overlap by itself should be held only as a most qualitative idea, since molecule formation can be regarded as a competition between many factors of comparable importance, one of which is the procurement of large bond overlap.
3. Individual study of the many three-center integrals involved in these calculations indicates that more reliable approximations than the usual ones are worthy of investigation.
4. The SCF MO's are in relatively good agreement with qualitative considerations of the electronic structure of H_2O.
5. The SCF MO method which neglects MO-orthogonality, even with respect to inner-shell 1s electrons, gives results which are significantly different from those of the more complete treatment.
6. The SCF MO energies are found to be in as good

agreement with experiment as can be expected. One must take into account the fact that the orbital and total energies were differences between quantities each of which has an error comparable to the differences sought.

7. In the approximation utilized, configuration interaction (CI) was found to be unimportant with respect to the MO ground state wave function.
8. Comparisons of the SCF MO's with orbitals found by other methods was found to be quite encouraging.
9. Calculations were performed to determine the nature of the first excited singlet state of H_2O. The transition probability results were found to correlate relatively well with experiment.
10. The effect of error in the three-center integrals on the SCF calculations was found to be of significance.

V. SUMMARY

The first part of the thesis included a brief general description of the two approximations, the molecular orbital (MO) and valence bond (VB) methods, which are generally utilized in treating problems of electronic structure. The historical application of these methods to the water molecule was then reviewed and discussed in some detail. The more recent qualifications of these early treatments were described and found to yield quite satisfactory qualitative explanations for the electronic properties of H_2O.

Chapter III included the general formulation of the present SCF LCAO MO treatment of H_2O, the evaluation and approximation of integrals involved in the calculations, and the presentation of the results and interpretations thereof.

Chapter IV gave a brief list of the major conclusions derived from this work.

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VIII. APPENDICES

A. The Evaluation of (0:h'h")

M. P. Barnett and C. A. Coulson (92) have given a general infinite series expansion of the function

$$r_b^{m-1} \exp(-\beta r_b) \qquad (A.1)$$

in terms of r_a and θ_a. The explicit formulation includes products of ordinary Legendre polynomials and certain other functions which are derived from standard bessel functions of half integral order and purely imaginary argument. This series was substituted for h' and h" in the integral (0:h'h"). The resulting expansion, after integration over θ and ϕ, may be written as follows:

$$(0:h'h") = \sum_{n=0}^{\infty} 4\mu R^{-1}(2n+1)P_n(\cos\gamma) \int_0^{\infty} [p_n(1, \mu r, \mu R)]^2 dr , \qquad (A.2)$$

where the function in the integral is defined in reference (92). Utilizing this definition, the expansion was formulated in terms of integrals of the following form:

$$X_n = \int_0^R I_n^2(r) r^2 dr \qquad (A.3)$$

Table 23. The series expansion of (O:h'h")

	H-O-H bond angle (degrees)						
n	0	90	100	105	110	120	180
0	0.27715	0.27715	0.27715	0.27715	0.27715	0.27715	0.27715
1	0.16114	0	-0.02798	-0.04171	-0.05511	-0.08057	-0.16114
2	0.05054	-0.02527	-0.02298	-0.02019	-0.01640	-0.00632	0.05054
3	0.01465	0	0.00362	0.00505	0.00605	0.00641	-0.01465
4	0.00572	0.00215	0.00152	0.00082	-0.00002	-0.00165	0.00572
5[a]	0.00145	0	-0.00041	-0.00050	-0.00048	-0.00013	-0.00145
Total	0.51065[b]	0.25403	0.23092	0.22063	0.21119	0.19489	0.15618

a. By graphical extrapolation.

b. Exact value: 0.51084.

$$Y_n = \int_0^R I_n(r)\, I_{n+2}(r) r^2 dr$$

$$X_n' = \int_R^\infty K_n^2(r)\, r^2 dr \qquad (A.3)$$

$$Y_n' = \int_R^\infty K_n(r)\, K_{n+2}(r) r^2 dr \ .$$

It may be shown for both primed and unprimed functions that

$$X_n = (2RL_n + Y_{n-1})/3$$

and (A.4)

$$Y_n = \left[3nX_n - 3(n+1)Y_{n-1} + 2(n+1)RL_{n+1}\right]/(2n+1) \ ,$$

where $L_n = \int_0^R I_n^2(r) r dr$. The latter integral may be evaluated from the bessel equation (115).

Analytical evaluations of the X_n and Y_n for small n were carried out to ten significant figures. Equations (A.4) were then utilized to evaluate higher integrals. The bessel functions were evaluated explicitly for the desired parameters given by Barnett and Coulson. The numerical results of the series expansion are given in Table 23.

B. The Evaluation of (h'h":s's') and (h'h":z'z')

These evaluations were based upon K. Rüdenberg's expansion method for three- and four-center integrals (101). They are based upon the expansion of h' and h" in terms of a complete orthogonal set of AO's on the oxygen atom, which may be formulated as follows:

$$h = \sum_{j=0} \sum_{n=j+1} S[h,x(nj)]\, x(nj) \quad . \qquad (B.1)$$

The set of function x(nj) are constructed from ordinary Slater AO's. These are automatically orthogonal for different values of j, but linear combinations must be taken to form an orthogonalized sub-set with constant j.

The overlap integrals over Slater AO's were maximized with respect to parameter Z contained in each. In this manner, it was hoped to secure maximum rapidity of convergence of the series.

Equation (B.1) was substituted into the integrals, yielding a series involving the overlap and mononuclear repulsion integrals. These were then evaluated by standard methods to yield the results given in Table 24 for the H-O-H bond angle of zero degrees. For other bond angles, each term is multiplied by $P_j(\cos\gamma)$ in the same

Table 24. The evaluation of (h'h":s's') and (h'h":z'z')

		(h'h':z'z')		(h'h':s's')	
j	n	Subtotal	Total	Subtotal	Total
0	1	0.26683		0.26070	
	2	-0.02343		-0.02196	
	3	0.02915	0.27255	0.02525	0.26399
1	2	0.16532		0.15339	
	3	-0.00211		0.00077	
	4	-0.00362	0.15959	-0.00653	0.14763
2	3	0.05792		0.04908	
	4	0.00311		0.00087	
	5	0.00017	0.06121	0.00014	0.05009
3	4	0.01800		0.01418	
	5	0.00041		0.00122	
	6	-0.00191	0.01650	-0.00213	0.01327
Total			0.50984		0.47498
Exact			0.51029		0.48061

manner as for (0:h'h").

The Rüdenberg method is quite difficult to carry out because of the cumbersome orthogonalization requirements. Furthermore, the convergence of the series over n seems to be quite erratic. The Barnett-Coulson method (92) is probably better in this respect since the double series is reduced to a single series.

C. The Charged Sphere Repulsion Formulas

The following formulas were derived by standard integrations of the classical repulsion between uniform charge distributions. The more complicated integrations were carried out in cylindrical coordinates.

The first case is the most general, that of two intersecting uniformly charged spheres of different radii, R_1 and R_2, the centers of which are at a distance R_o apart:

$$\begin{aligned} E = Q_1Q_2(160)^{-1}R_1^{-3}R_2^{-3}R_o^{-1}[&5(R_1^6 + R_2^6) - R_o^6 \\ &+ 30R_oR_1^2R_2^2(4R_1 + 4R_2 - 3R_o) + 80R_2^3R_1^3 \\ &- 40R_o^3(R_1^3 + R_2^3) - 24R_o(R_1^5 + R_2^5) \\ &+ 45R_o^2(R_1^4 + R_2^4) - 45R_1^2R_2^2(R_1^2 + R_2^2) \\ &+ 15R_o^4(R_2^2 + R_1^2)] \ . \end{aligned} \qquad (C.1)$$

For the special case of equal radii, (C.1) may be written

$$E/(Q_1Q_2) = 6/(5R_1) - (160)^{-1}R_1^{-6}\left[80\ R_o^2R_1^3 - 30\ R_o^3R_1^2 + R_o^5\right] . \quad (C.2)$$

If $R_1 < R_2$, and if the smaller sphere is contained entirely within the large, the repulsion may be written

$$E = Q_1Q_2(10)^{-1}R_2^{-3}\left[15R_2^2 - 3R_1^2 - 5R_o^2\right] . \quad (C.3)$$

If R_o is equal to zero

$$E = 3Q_1Q_2(10)^{-1}R_2^{-3}\left[5R_2^2 - R_1^2\right] . \quad (C.4)$$

If the spheres have equal radii and are directly superposed,

$$E = 6/(5R_2) . \quad (C.5)$$

The repulsion between a spherical distribution and a point charge within it is given by

$$E = 2^{-1}R_1^{-3}(3R_1^2 - R_o^2) , \quad (C.6)$$

where R_o is the distance of the point from the center of

the sphere.

If the point charge is on the surface of the sphere, or outside of the sphere,

$$E = 1/R_o \ . \qquad (C.7)$$

If the point charge is at the center of the sphere,

$$E = 3/(2R_1) \ . \qquad (C.8)$$

Finally, if two charged spheres do not overlap, their repulsion is given by equation (C.7).

D. The Dipole Moment Integrals

The dipole moment of H_2O may be expanded by using suitable transformations so as to be expressed in terms of simple integrals over AO's. The general formulas for these integrals, together with their numerical values for the parameters used in H_2O are given as follows:

$$\int 1s_a z 2pz_a' dv = 32\mu^{3/2}\mu'^{5/2}(\mu + \mu')^{-5} = 0.0540$$

$$\int 2s_a' z' 2pz_a' dv = (5)(3)^{1/2}6^{-1}\mu_a^{-1} = 0.6345$$
(for equal μ-values)

$$\int 1s_a z 1s_b dv = 8^{-1}R_4\mu_a^{3/2}\mu_b^{3/2}(A_3B_1 - A_1B_3) = 0.0512$$

$$\int 1s_a \underline{z}\, 2s_b' dv = 16^{-1} 3^{-1/2} \mu_a^{3/2} \mu_b^{5/2} R^5 (A_4B_1 - A_2B_3 - A_3B_2 + A_1B_4) = 0.1270$$

$$\int 1s_a \underline{z}\, 2pz_b' dv = 16^{-1} \mu_a^{3/2} \mu_b^{5/2} R^5 (A_3B_1 - A_1B_3 - A_4B_2 + A_2B_4) = -0.2847$$

$$\int 1s_a \underline{y}\, 2py_b' dv = 32^{-1} \mu_a^{3/2} \mu_b^{5/2} R^5 [A_4(B_o - B_2) + A_2(B_4 - B_o) + A_o(B_2 - B_4)] = 0.3561 .$$

The z-direction is taken along the molecular axis. The origin of $\underline{z}$ and $\underline{y}$ is taken to be at the mid-point between a and b, the positive direction of $\underline{z}$ being towards b. The positive lobe of $2pz_b$ is directed towards a. The argument of A_n is $\frac{1}{2}R(\mu_a + \mu_b)$; that of B_n is $\frac{1}{2}R(\mu_a - \mu_b)$. Tables and recusion formulas are given by Kotani (90).